

AMERICAN CHEMICAL JOURNAL

[Contribution from the Chemical Laboratory of the University of Wyoming.]

THE REPLACEMENT OF HALOGEN BY THE NITRO GROUP.

[SECOND PAPER.]

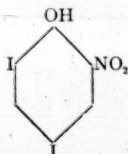
BY L. CHAS. RAIFORD AND FRED. W. HEYL.

In a recent paper¹ we recorded the results of experiments in which an attempt was made to determine the relative activity toward nitrous acid of two of the symmetrical trihalogenated phenols, 2,4,6-tribromphenol and 2,4,6-trichlorphenol. The work was undertaken for the purpose of comparing the action of these compounds with the behavior of the corresponding halogenated *m*-cresols, the bromine compound of which had been found very reactive, giving a pair of isomeric mononitrodibrom-*m*-cresols, while the chlorine derivative was totally inactive under the same conditions. The reactivity of the halogenated phenols showed the same differences where the same halogens were involved, but the yields of the isomers obtained were much smaller than in the case of the cresols.

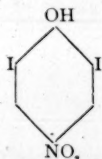
In view of these facts it became a matter of interest to examine the behavior of an iodine compound of this series. Accordingly, 2,4,6-triiodphenol was selected. Treatment of

¹ THIS JOURNAL, 43, 393 (1910).

this with nitrous acid in the manner specified below produced the two isomeric mononitrodiiodphenols:



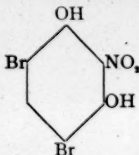
4,6-Diiod-2-nitrophenol,
melting at 98°.



2,6-Diiod-4-nitrophenol,
melting at 155°.

It is of interest here, also, to note that during this reaction more iodine was liberated than can be accounted for by the formation of a mononitrodiiod compound only, and that this indicates the possible production of some dinitromonoiiodphenol. A second observation, which shows that triiodphenol is more reactive than the corresponding bromine compound, under the conditions of this nitration, is the fact that with the iodine compound a much smaller amount of unaltered substance was recovered from the reaction mixture.

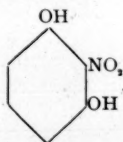
In a second set of experiments it was decided to study the behavior of a trihalogenated phenol containing two hydroxyl groups, and for this purpose 2,4,6-tribromresorcinol was chosen. When this compound was nitrated by the method used in these experiments, but a single nitro body was formed—a mononitrodibromresorcinol, melting at 148°. The only compound of this composition recorded by Beilstein was isolated by Weselsky and Benedikt,¹ who reported the melting point as 117°, and the structure as 4,6-dibrom-2-nitroresorcinol,



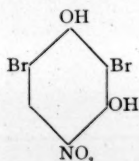
They obtained this compound by brominating a mononitro-

¹ Monats. Chem., 1, 886 (1881).

resorcinol which they found to be volatile with steam, and to which, on the basis of analogy to the volatile mononitrophenol, they assigned the formula



If the formulas assigned to these substances are correct, then our new nitro compound must be 2,6-dibrom-4-nitroresorcinol, and should be represented by the formula



The compound has been characterized by the preparation of several derivatives, and ultimately we shall determine the position of the nitro group. The results so far obtained are published at present because our work is now about to be interrupted for several months.

Further work has been outlined with the nitro compounds mentioned above, as well as with tribromacetanilide which, thus far, we have been unable to nitrate with nitrous acid; and with benzoyl-2,4,6-tribromanilide, which, according to Borrelli,¹ interacts with nitric acid to give two isomeric dinitro derivatives in which all the bromine is retained.

EXPERIMENTAL PART.

Preparation of Starting Material.—2,4,6-Triiodphenol was prepared by the method of Messinger and Vortmann,² which consists in a rearrangement of diiodphenoliod whereby the iodine atom bound to oxygen migrates to the ring. The

¹ Gazz. chim. ital., **17**, 527.

² Ber. d. chem. Ges., **22**, 2313.

change was brought about by boiling the diiod compound with a dilute solution of potassium hydroxide. From the resulting liquid, after filtration, quite pure triiodphenol was precipitated by the addition of hydrochloric acid. Crystallization from alcohol gave a pure product melting at 158° .¹

Messinger and Vortmann¹ give 156° as the melting point.

Analysis for iodine gave the following results:

0.1706 gram substance gave 0.2559 gram AgI.

	Calculated for $C_6H_3OI_3$	Found.
I	80.72	81.04

2,4,6-Triiodphenyl Acetate.—The triiodphenol used in the nitration specified below was further identified by the preparation of an acetyl derivative. A portion of the substance weighing three grams was mixed with an equal weight of anhydrous sodium acetate, and the mixture heated gently with an excess of acetic anhydride, after which it was allowed to stand overnight. From the resulting solid, triiodphenyl acetate was extracted by boiling benzene, and from the solution obtained there separated colorless needles which after two further crystallizations from benzene melted sharply to a clear oil at 154° . A sample crystallized from chloroform melted at the same point. Analysis for iodine gave the following result:

0.2435 gram substance gave 0.3360 gram AgI.

	Calculated for $C_8H_5O_2I_3$	Found.
I	74.12	74.55

Nitration of 2,4,6-Triiodphenol.—In the experiments with triiodphenol it was early observed that this substance was not very soluble in glacial acetic acid at the temperature (12° – 15°) at which these nitrations have been carried out; and subsequent tests showed that if acetic acid was added in sufficient quantity to prevent crystallization of triiodphenol during nitration, the volume of water into which the reaction mixture must be poured was so large that isolation of the nitro compounds involved much time and trouble.

¹ *Loc. cit.*

To avoid this difficulty a portion of the acetic acid was replaced by benzene, which readily dissolved triiodphenol and did not interfere with the reaction.

Twenty-one and nine-tenths grams of triiodphenol was dissolved in a mixture of 100 cc. glacial acetic acid and 200 cc. benzene. This liquid was cooled to 12° – 15° and enough benzene added to dissolve any solid that had crystallized out. To this solution was next added, during half an hour, a ten per cent. excess of sodium nitrite, while the mixture was frequently shaken and the temperature carefully kept between 12° and 15° . The reaction mixture was allowed to stand overnight. At this point a portion of the liquid was removed, and the iodine that had been liberated during the reaction was shaken out with chloroform and titrated with standard solution of thiosulphate. The calculation showed that about five per cent. more iodine had been set free than was required by the production of a mononitrodiiod compound only, and this was thought to indicate the possible formation of a small amount of a dinitro derivative. The benzene was removed from the remainder of the mixture by evaporation under reduced pressure, and the residue, consisting chiefly of the glacial acetic acid solution of the nitro products, was poured into cold water. A black oil separated, which upon cooling congealed, and when removed from the greater part of the water and placed on a clay plate, finally solidified. The crude product weighed 15.7 grams, and its indefinite melting point indicated a mixture of substances.

Separation of the Isomers.

The Ortho Compound.—The method of separation used with the isomeric nitrodibromphenols, which involved the difference in solubility of the two substances in a mixture of chloroform and ligroin, was at first tried with the iodine derivatives, but it gave unsatisfactory results. The entire mass of crude product was next converted into potassium salts by boiling with one liter of aqueous solution containing 2.3 grams (one molecule) of potassium hydroxide. The two potassium salts thus formed were separated by a careful

systematic fractional crystallization. The salt of 4,6-diiod-2-nitrophenol separated first in the form of reddish brown needles that were practically pure. A portion was recrystallized from water, and after being dried to constant weight at 110° was analyzed for iodine.

0.2683 gram substance gave 0.2945 gram AgI.

	Calculated for $C_6H_2O_2NI_2K$.	Found.
I	59.17	59.30

The first five fractions of this potassium salt, which together weighed about four grams, were separately decomposed by dilute hydrochloric acid, and each gave the mononitro-diiodphenol described by Körner,¹ which melts at 98° . From alcohol the compound crystallized in the form of bright yellow needles, which upon analysis for iodine gave the following results:

0.1318 gram substance gave 0.1582 gram AgI.

	Calculated for $C_6H_2O_2NI_2$.	Found.
I	64.93	64.85

Hydrochloride of 4,6-Diiod-2-aminophenol.—The *o*-nitro-diiodphenol mentioned above was still further characterized by the preparation of its reduction product, which has not been described. This was secured as follows: The nitro compound was dissolved in the smallest possible quantity of boiling alcohol, and to the hot solution one-fourth more than the calculated amount of stannous chloride dissolved in concentrated hydrochloric acid (1 gram—1 cc.) was added. The mixture was then boiled until the color of the nitro body had been about discharged, after which an equal volume of concentrated hydrochloric acid was added and the whole allowed to stand. Upon cooling, the amino hydrochloride separated out. It was collected on a filter, dissolved in water, in which it is very soluble, and recrystallized by the addition of hydrochloric acid. In this way it was repeatedly crystallized until it was free from tin salt, when it separated in elongated prisms.

¹ Jahres. d. Chem. 1867, 617.

These were dried for several days over potassium hydroxide and then analyzed for halogen.

0.2279 gram substance gave 0.3518 gram AgHal.

Halogen	Calculated for	Found.
	$C_6H_6ONClI_2$	
	72.80	72.83

The Para Compound.—When the filtrate from the salt of the ortho compound was evaporated it left a mass of greenish crystals that proved to be the potassium salt of the para compound. This was repeatedly fractionated, and the purest product thus obtained was decomposed by dilute hydrochloric acid, liberating 2,6-diiod-4-nitrophenol, which melted at about 150° . By several recrystallizations of this from alcohol it was obtained in nearly colorless prisms that melted sharply at 155° , and which gave the following results when analyzed for halogen:

0.1626 gram substance gave 0.1930 gram AgI.

I	Calculated for	Found.
	$C_6H_3O_3NI_2$	
	64.93	64.18

The filtrate from the potassium salt of the para compound was acidified with dilute hydrochloric acid and gave a solid melting at 156° . A mixture of this substance and pure triiodphenol melted at the same temperature as either of them separately, which showed that the substance in question was unaltered triiodphenol. The amount recovered was much smaller than when tribromphenol was nitrated.

Nitration of Tribromresorcinol.—2,4,6-Tribromresorcinol¹ was prepared by mixing aqueous solutions of bromine and resorcinol in the theoretically required proportions, and was repeatedly crystallized from water until it melted constantly at 112° . Eleven and one-half grams of this product was dissolved in about twenty-five times its weight of glacial acetic acid, the solution cooled to 12° – 15° , and then treated with sodium nitrite as already described. When about two-thirds of the nitrite had been added, a nitro compound (see below)

¹ Hlasiwetz and Barth: Ann. Chem. (Liebig), **130**, 357.

began to crystallize out. When all had been added and the mixture had been allowed to stand for half an hour in a cool place, the crystals, which after drying weighed three and one-half grams, were collected on a filter, and then crystallized twice from water, from which they separated in orange-colored needles melting at 148° . The acetic acid filtrate was now poured into five volumes of water, when a brown precipitate was formed. After standing some hours the mixture was filtered. The dried precipitate weighed 2.2 grams and contained 57.05 per cent. bromine, but since it did not have a sharp melting point and could not be obtained in crystal form, it was not further investigated. The filtrate was acidified with dilute sulphuric acid and extracted with chloroform. Evaporation of the latter left 3.6 grams of a brown residue which proved to be a mixture of tarry matter and a substance which could be crystallized from water, and was identical with the nitro compound mentioned above.

Analysis for bromine gave the following results:

0.2041 gram substance gave 0.2474 gram AgBr.

	Calculated for $C_6H_5O_4NBr_2$	Found.
Br	51.11	51.44

This nitro compound is acid in character, as shown by the salt formation specified below, and is nonvolatile with steam. It is readily soluble in alcohol, ether, chloroform, and benzene, but characteristic crystals could not be obtained from any of these liquids. From 30 per cent. alcohol maroon-colored prisms that melted at 148° were secured. Mixing these with the orange-colored needles caused no depression of the melting point. Analysis for bromine likewise indicated that the products were the same.

0.2434 gram substance gave 0.2905 gram AgBr.

	Calculated for $C_6H_3O_4NBr_2$	Found.
Br	51.11	50.80

Ammonium Salt of Dibromnitroresorcinol.—An attempt was made to further characterize this dibromnitroresorcinol by the

preparation of its salts. It forms sodium and potassium salts very readily, but both are so soluble that satisfactory crystals could not be obtained. A portion was dissolved in warm ammonia water and the solution allowed to stand in a warm place for several days. Upon evaporation of the excess of liquid, deep yellow prismatic crystals, that were free from water of hydration, were deposited. These were crystallized from water several times, dried to constant weight at 110° , and then analyzed for bromine. The results indicated a monoammonium salt.

0.1476 gram substance gave 0.1683 gram AgBr.

	Calculated for		Found.
	$C_6H_9O_4N_2Br_2$	$C_6H_9O_4N_2Br_2$	
Br	46.10	48.48	48.52

Hydrochloride of Dibromaminoresorcinol.—Five grams of the above nito compound were dissolved in hot alcohol and reduced with a hydrochloric acid solution of stannous chloride in the manner already described. The product that crystallized out was purified by treatment of its warm aqueous solution with concentrated hydrochloric acid, this process being repeated until the substance was practically colorless and no longer responded to a test for tin. It was dried for several days over potassium hydroxide and then analyzed for halogen and for nitrogen:

0.1792 gram substance gave 0.2912 gram AgHal.

0.1846 gram substance required 11.5 cc. 0.05 N HCl.

Halogen	Calculated for		Found.
	$C_6H_7O_2NClBr_2$		
	61.18		61.18
N	4.38		4.36

Dibromaminoresorcinol.—The first attempt to prepare this free base was made by mixing with a water solution of the hydrochloride a slight excess of ammonium carbonate. A dark liquid, but no precipitate resulted. When a solution of the hydrochloride was mixed with a solution containing the theoretically required amount of sodium bicarbonate, the free amine was promptly precipitated in the form of a gray powder.

This was at once collected on a filter, washed several times with cold water, and then dried on a clay plate. From benzene the substance crystallized in prisms that were at first colorless, but which soon changed to gray. When heated above 135° it began to darken in color, and continued to blacken with rise in temperature; above 175° it decomposed without melting. Analysis for bromine gave the following results:

0.1419 gram substance gave 0.1897 gram AgBr.

	Calculated for $C_9H_9O_2NBr_2$	Found.
Br	56.53	56.88

Acetylaminodibromresorcinylic Diacetate.—This acetyl derivative was most conveniently prepared directly from the amino hydrochloride as follows: Equal weights of the hydrochloride and anhydrous sodium acetate were pulverized together, and upon this powder, in a small flask, was poured twice the theoretically required amount of acetic anhydride. Reaction began at once, as was indicated by a sharp rise in temperature, after which the mixture was boiled gently for about five minutes, and then set aside for twenty-four hours. At the end of this period the resulting solid was shaken with enough water to dissolve the sodium acetate, and the residue collected on a filter. Repeated crystallization from alcohol gave colorless hexagonal plates that melted at 174° – 175° . The substance did not dissolve in a solution of sodium hydroxide and was regarded as a diacetate. Analysis for bromine confirmed this view:

0.1715 gram substance gave 0.1581 gram AgBr.

	Calculated for $C_{13}H_{11}O_6NBr_2$	Found.
Br	39.12	39.23

Picrate of Dibromaminoresorcinol.—The picrate of this amine was obtained by dissolving a portion of the hydrochloride in a saturated solution of picric acid and then allowing the mixture to stand. In a short time crystals in the form of dark green scales appeared. These were recrystallized from water in which they readily dissolve upon heating. When the sub-

stance was heated to 220° it began to decompose without melting. It was analyzed for bromine:

0.2156 gram substance gave 0.1552 gram AgBr.

Br	Calculated for	Found.
	$C_{12}H_9O_3N_2Br_2$	
	31.23	30.63

Work has been outlined on the chlorine and iodine derivatives of resorcinol.

LARAMIE, WYOMING,
May, 1910.

ON THE REARRANGEMENT OF THE TAUTOMERIC
SALTS OF 1,4-DIPHENYL-5-THIONURAZOLE
AND 1,4-DIPHENYL-5-THIOLURAZOLE.

[SEVENTEENTH COMMUNICATION ON URAZOLES.]

BY SIDNEY NIRDLINGER AND S. F. ACREE.

(We are indebted to the Carnegie Institution of Washington for aid in our research on tautomerism.)

Tautomeric compounds may be roughly classified under two heads;¹ first, those in which the equilibrium between the different forms is established very quickly in comparison with the velocity of the particular reaction being studied, and, second; those in which the equilibrium is established at a rate comparable with that of the reaction. The ideas of tautomeric equilibrium and especially of tautomeric salts, advanced by Acree² and collaborators, have made possible the quantitative study of the first case with results entirely in harmony with the theory. While the slow rearrangement of tautomeric acids and their final states of equilibrium have been measured by several investigators, no quantitative work has been done on the tautomeric salts of such acids, especially in the light of the theory of Acree. Such work should give a severe test for this idea and the results should be conclusive one way or the other. The most important work

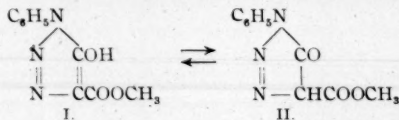
¹ See THIS JOURNAL, **43**, 361, 424.

² *Ibid.*, **37**, 71; **38**, 1; **39**, 124, 226. Ber. d. chem. Ges., **41**, 3199.

along this line has been done by Wislicenus,¹ Dimroth,² and Michael.³

Wislicenus, working on formylphenylacetic ester, was able to isolate a liquid enol and a solid keto form,⁴ and to measure roughly the equilibrium between the two in a number of cases. He found that nondissociating solvents were favorable to that form which he called the enol or weaker acid form. The greater the concentration the more enol form he found in the solution. Starting with either form, under the same conditions of temperature and concentration, he found that the solutions are the same at the end of the reaction, thus showing that the rearrangement is perfectly reversible. His work on the salts was not very conclusive. The sodium salt made from either form liberated the so-called enol ester when precipitated with carbon dioxide, while with sulphuric acid the keto ester was liberated. Two different copper salts were also made but their exact constitution is doubtful.

The work of Dimroth⁵ on methyl 1-phenyl-5-hydroxy-1,2,3-triazole-4-carboxylate was more conclusive owing to the fact that both tautomeric forms are stable solids, which in solution attain the following equilibrium:



The enol form (I) is a strong acid and liberates iodine quantitatively from potassium iodate and iodide in acid solution, while the keto form (II) is practically neutral. Dimroth found that the amount of the strongly acid enol form was greatest in the strongly dissociating solvents, this being in harmony with Wislicenus' results. In water, for example, the ratio of enol to keto is 1 : 14, in methyl alcohol 1 : 150,

¹ Ann. Chem. (Liebig), **291**, 147. Ahrens' Sammlung. II, 187.

² Ann. Chem. (Liebig), **335**, 1; **338**, 143.

³ Michael and Hibbert: Ber. d. chem. Ges., **41**, 1080.

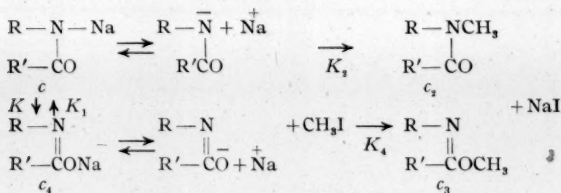
⁴ This was afterwards shown by him, and also by Michael, to be a mixture.

⁵ Loc. cit.

in ethyl alcohol 1 : 300, while in chloroform, ether, etc., only the merest trace of enol form was found. An interesting fact observed was that the equilibrium was independent of temperature and concentration. In regard to the rate of rearrangement it was found that the change of the enol into the keto form was greatest in nonaqueous solvents, showing that the reaction was not due to the addition and splitting out of water. The molecular forms of the acids and not the anions were thought to be in direct equilibrium, as was also thought by Acree¹ to be true in the case of the salts of the urazoles, although the evidence for this is very meagre. No work could be done with the salts, as the keto ester is practically a nonelectrolyte and does not form stable salts.

Michael and Hibbert came to the conclusion that there is no direct connection between the equilibrium point, or velocity of change, of two tautomers and the physical constants of the solvents, such as the dielectric constant.

As we see, the work of Wislicenus, Dimroth, and Michael and Hibbert was concerned simply with the study of the rate of rearrangement and equilibrium of the acids themselves, and no attempt was made to study quantitatively and systematically the action of alkylating agents or other substances on either of the acids or their salts, or on an equilibrium mixture of the two. This is not a simple problem, as is shown by the following considerations:



In this scheme c is the original concentration of the keto form, c_4 that of the enol form, c_1 the amount of keto salt trans-

¹ THIS JOURNAL, **38**, 1. Wegscheider: Z. physik. Chem., **35**, 518; **36**, 543. Goldschmidt: Z. Elek. Chem., **11**, 5. Dimroth: *Ibid.*, **11**, 137.

formed into enol, c_2 the concentration of the keto ester, and c_3 that of the enol ester. Taking the simplest case first, suppose an equimolecular amount of methyl iodide is added to a solution containing a mixture of the two salts. We would have the following three reactions taking place:

- (a) Sodium keto salt $\rightleftharpoons$ sodium enol salt.
- (b) Sodium keto salt and $\text{CH}_3\text{I} \rightarrow$ methyl keto ester and NaI .
- (c) Sodium enol salt and $\text{CH}_3\text{I} \rightarrow$ methyl enol ester and NaI .

These would be represented by the differential equations:

$$\frac{dc_1}{dt} = K(C - C_1 - C_2) - K_1(C_4 + C_1 - C_3)$$

$$\frac{dc_2}{dt} = K_2(C - C_1 - C_2)(C + C_4 - C_2 - C_3)$$

$$\frac{dc_3}{dt} = K_4(C_4 + C_1 - C_3)(C + C_4 - C_2 - C_3)$$

In these equations K is the velocity constant for the change of keto salt into enol salt, K_1 the constant for the reverse rearrangement, K_2 that for the formation of keto ester, and K_4 that for the formation of enol ester. The integration of these three equations would give a complete solution of the problem. This was not attempted, as the simultaneous alkylation and rearrangement was not studied. The differential equations for the case in which the salt rearrangement is not reversible, as well as for those in which the esters rearrange, have been worked out, but as they were not used in the work reported now, they will not be given. The above equations do not take into consideration the question whether the rearrangements or the alkylation reactions of the two tautomeric salts are ionic, or molecular, or both, side by side. If, however, the principle of isohydric solutions holds, the ratio of the concentration of the anions to that of the molecular salt should not change appreciably for either of the two forms in the solution, as we have sodium iodide formed in an amount equivalent to the sum of the keto

and enol salts disappearing by esterification. Then the different constants used above would equal the real reaction constants multiplied by α or $1-\alpha$, according as the reactions are ionic or molecular or both, where α is the percentage of ionization. Then, for example, $K = (1 - \alpha) K'$, $K_1 = \alpha K'_1$, or $K_2 = K'_2 \alpha + K''_2(1 - \alpha)$, when K' , K'_1 , K'_2 and K''_2 are the true constants.

It is assumed that the rearrangement of the salt is a monomolecular reaction, as that seems to be made most probable by our work, described below, and that of Mr. E. P. Doetsch. The possibility, however, that the rearrangement is due to a union of the ions in the solution with the molecular form of the salt, or to other complex reactions, is not excluded, and this possibility is being investigated. In this case the rearrangement would not be monomolecular, although in some cases it might still apparently be so.¹

The study of the slow attainment of equilibrium between the two forms of a weakly acid tautomeric substance should give most conclusive evidence as to the question of abnormal hydrolysis in the more concentrated solutions.² If we should add a solution containing an equilibrium mixture of the sodium salts, for example, to a solution of an equilibrium mixture of the free acids, we could easily calculate the total amount of each form in the solution, provided there was no abnormal hydrolysis. We could in some cases use conductivity methods. In other cases the whole mixture could be alkylated very quickly and the ratio of esters determined. If we have abnormal hydrolysis, the calculated should differ from the experimental values by an amount depending on the difference between the affinity constants of the two forms, the equilibrium constants, etc. The possibility of the influence of double salts, complex molecules, solvates, etc., must be carefully considered.

The compounds that first suggested themselves as being easily obtainable for our work were Dimroth's two forms³

¹ Acree and Nirdlinger: *THIS JOURNAL*, **43**, 358. Julius Meyer: *Z. physik. Chem.*, **66**, 81; **67**, 257.

² *THIS JOURNAL*, **43**, 365.

³ *Ann. Chem. (Liebig)*, **336**, 1.

of methyl 1-phenyl-5-hydroxy-1,2,3-triazole-4-carboxylate. The enol form is a strong acid while the keto form is practically neutral. This would make it necessary, in esterifying a mixture of the two forms, to separate the keto form from the neutral ester formed, by converting it into the enol and extracting with an alkali. It was found that by rapid work the enol acid could be easily extracted from chloroform or ethereal solutions by means of aqueous solutions of potassium hydroxide, and the keto acid could be easily converted into the enol acid and extracted by treating the mixture with alcoholic solutions of potassium hydroxide. When the methyl enol ester, however, was treated by this method it was saponified to a considerable extent. For example, 0.1282 gram keto form and 0.1065 gram methyl enol ester were dissolved in chloroform, the chloroform evaporated, and the residue taken up in alcoholic potash. Then water was added and the solution extracted with chloroform and only 0.2 milligram of extracted substance was obtained. In another case from 0.1870 gram ester only 0.0059 gram of extract was obtained. In still another case in which the solutions were carefully cooled 0.1011 gram ester gave back 0.0672 gram unchanged ester. On this account the work had to be given up.

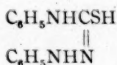
The compounds finally chosen for this work were the 1,4-diphenyl-5-thionurazole and 1,4-diphenyl-5-thiolurazole first described by Marckwald¹ and later by Busch² and his collaborators. A short summary of the evidence for the constitution of these compounds is necessary as our work has shown that the constitutions previously given are wrong. We should like to state at once that the work with these 5-thio-urazoles is much more difficult than any that we have yet done. The properties of the compounds do not allow the development of very accurate quantitative methods, and added complications, due to the tautomeric changes going on, make the slow progress of the work sometimes very discouraging. Since these are the very phases of tautomerism that we wish

¹ Ber. d. chem. Ges., **25**, 3098; **29**, 2920.

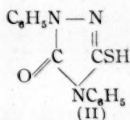
² Holzmänn: Diss., Erlangen, 1902.

now to study, however, we shall continue the investigation of the problem.

W. Marckwald¹ found that by the action of phenylhydrazine on phenyl mustard oil in the cold, an α -diphenylthiosemicarbazide was formed which melted at 139° and then rearranged into the β -semicarbazide melting at 176° described by E. Fischer.² Marckwald gave to this α -semicarbazide formula (I) and the constitution of the thiourazole formed



(I)



(II)

by treating this with phosgene in the cold was thought to be represented by formula (II). This urazole melted at 219° – 221° when crystallized from *hot* alcohol, and when treated with methyl iodide yielded an ester melting at 185° (196° is the true melting point). This ester gave methyl sulphhydrate and the salt of 1,4-diphenylurazole when it was treated with potassium hydroxide, a reaction which showed that the methyl is attached to the sulphur atom. These points, especially the crystallization from *hot* alcohol, which causes a rearrangement, should be noted, as they are of considerable importance.

In the first papers³ by Acree on the urazoles, it was stated that work was in progress on the 3-thio (or hydroxy)-5-hydroxy (or thio)urazoles, but this was stopped at that time in favor of Professor Busch. But the evidence which Acree⁴ obtained proved beyond question that Marckwald's formulation for the constitution of the α - and β -thiosemicarbazides and the above-mentioned thiourazoles was wrong. It was proved that the α -1-phenylmethylthiosemicarbazide assumed by

¹ *Loc. cit.*

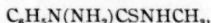
² *Ann. Chem. (Liebig)*, **190**, 122.

³ *THIS JOURNAL*, **27**, 126. *Ber. d. chem. Ges.*, **35**, 556; **36**, 3139.

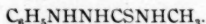
⁴ The work which I have done since 1901 on these thiourazoles will be published soon. Professor Busch has in the meantime done far more, and better, work on these substances and cleared up beautifully some of the questions which are of great importance in this series of tautomeric substances.

S. F. ACREE.

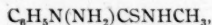
Marckwald to be the 1,4 compound, must be the 2,4 compound and have the formula



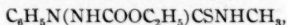
and that it rearranges, when heated in alcohol, especially in the presence of acids,¹ into the 1,4 compound having the formula



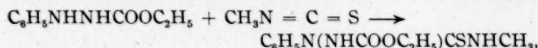
The proof, which was clear-cut, is the following: The α compound,



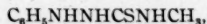
when heated with ethyl chlorcarbonate in chloroform solutions, with or without sufficient sodium bicarbonate to neutralize the hydrochloric acid liberated, gave the ester



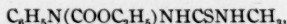
which, when treated with alkalis and then with an acid, yielded the 1-phenyl-4-methyl-3-hydroxy-5-thiourazole (A), which melted at 208° . This same ester was furthermore made by a reaction which could leave no doubt as to its constitution, namely, by the action of methyl mustard oil on phenyl carbazinic ester,



and when treated with alkalis as above it gave the same 1-phenyl-4-methyl-3-hydroxy-5-thiourazole, melting at 208° . But the β -phenylmethylthiosemicarbazide,

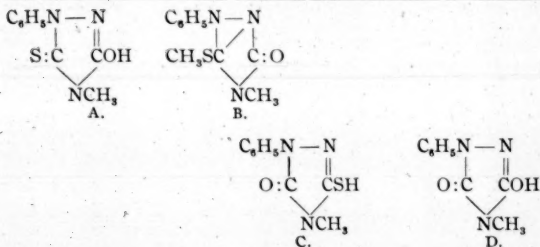


and ethyl chlorcarbonate in chloroform solution gave an isomeric ester,

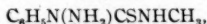


which, when treated with alkalis, etc., yielded an *isomeric* 1-phenyl-4-methyl-3-thiourazole (C), melting at 185° , which was also synthesized by an independent method.

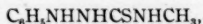
¹ Ber. d. chem. Ges., **25**, 3098. We ask that the study of this and similar rearrangements be left to us.



These two isomeric urazoles, (A) and (C), had therefore been synthesized by methods which could leave no doubt as to their constitution, or that the α -semicarbazide is the 2,4-phenylmethyl-3-thiosemicarbazide,



and that the β -semicarbazide is the 1,4-phenyl-3-thiosemicarbazide,



instead of the stereoisomeric forms of the 1,4-phenylmethyl-3-thiosemicarbazide as assumed by Marckwald.

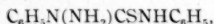
Furthermore, a comparison of the properties of our two isomeric 1-phenyl-4-methylthiourazoles left no doubt that Marckwald's 1,4-diphenylthiourazole melting at 221° was not a 3-thio compound, as assumed by him, but a 5-thio compound analogous to our 1-phenyl-4-methyl-5-thiourazole. The esters obtained by alkylating our 1-phenyl-4-methyl-5-thiourazole were certainly partially 5-thio alkyl compounds (B), because they gave a considerable quantity of 1-phenyl-4-methylurazole (D) and alkyl sulphhydrates when warmed with acid or alkaline solutions. They were therefore in every respect analogous to Marckwald's methyl ester melting at 184° (analogous to B), which he thought to be a 3-thiol methyl ester. That Marckwald's methyl thiol ester could not be a 3-thiol ester was further clear from the fact that of a large number of 3-thiol esters synthesized by Acree¹ by methods

¹ Ber. d. chem. Ges., **36**, 3139.

which left no doubt as to their constitution, *not one lost the alkyl sulphhydrate group to any appreciable extent when simply warmed with alkalis*, these compounds being particularly stable towards alkaline reagents.

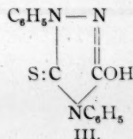
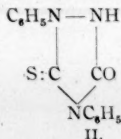
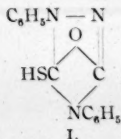
The evidence obtained by Acree shows conclusively then that Marckwald's so-called stereoisomeric thiosemicarbazides are the structurally isomeric 2,4- and 1,4-dialkyl-3-thiosemicarbazides, and that his so-called 1,4-diphenyl-3-thiourazole is in reality a 1,4-diphenyl-5-thiourazole.

But Busch¹ and Holzmann, in by far the best work then done on this problem, also came to the conclusion that the low-melting α -semicarbazide has the constitution



which is, chiefly because of their work, generally accepted to-day.

These chemists and other coworkers obtained by the action of phosgene on the α -diphenylthiosemicarbazide, a urazole acid which they supposed to be a 5-thiol² urazole (I). It melted, without further treatment, at 141° , and at this temperature, or on recrystallization from hot alcohol, rearranged into another form, which they assumed to have the constitution (II) or (III), or to be perhaps an equilibrium mixture of the two. This substance melted at 219° – 221° , the fusion point of the compound obtained by Marckwald.

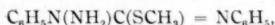


Busch and his colleagues believed that the low-melting urazole is a thiolurazole (I); because it yielded, when treated with methylating agents, the methyl thiol ester (IV), which

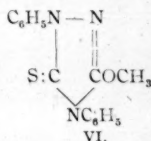
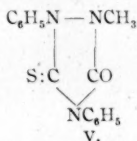
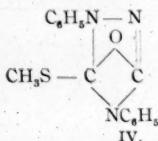
¹ Ber. d. chem. Ges., **34**, 326.

² See Ber. d. chem. Ges., **25**, 3098; **34**, 326, 340; **35**, 974. Holzmann: Diss., Erlangen, 1902. Grohmann: *Ibid.*, 1900. Reinhardt: *Ibid.*, 1906. Ilgen: Dissertation, Berlin, 1894.

lost methyl mercaptan easily when treated with potassium hydroxide. Furthermore, they obtained the same methyl thiol ester, having undoubtedly this constitution, by treating the thiomethyl- α -semicarbazide,



with phosgene.



Reinhardt proved that the two forms of the acid give different sodium salts. He tried to methylate the two salts with methyl iodide, but heated the reaction mixture to 100° in a sealed tube and, as a result, in both cases he obtained an ester, melting at 137° , free from sulphur, of 1,4-diphenylurazole. He¹ found that on treating the sodium salt of the low-melting acid with dimethyl sulphate, an oily mixture was obtained. This is an important observation and should be kept in mind. The sodium salt of the high-melting acid, which he thought to have the constitution (II) or (III), gave with dimethyl sulphate the ester before mentioned melting at 196° and known to have the constitution (IV), corresponding to the urazole (I). He explained this discrepancy by stating that, on account of the vigorous action of the dimethyl sulphate, the acid of formula (II) is transformed into (I), which is more easily methylated. The silver salt of the acid melting at 141° , when treated with methyl iodide,² gave an oil which was not easily crystallized. The silver salt of the acid melting at 221° , supposed to have the constitution (II), under the same conditions gave (1) a small amount of an ester melting at 133° - 134° , which did not split out mercaptan, and (2) much of the methyl thiol ester melting at 196° . This was also explained on the assumption that the silver is bound

¹ *Loc. cit.*, p. 72.

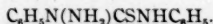
² *Loc. cit.*, p. 77.

partly to the sulphur, or that in the salt formation, some salt of the more reactive acid (I) was formed.

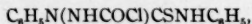
The work¹ described in the following pages was started provisionally on Busch's assumption that the low-melting acid has the composition (I) and the high-melting compound the composition (II). We were, however, soon forced to the conclusion that the low-melting acid is in reality 1,4-diphenyl-5-thionurazole, which can exist in two forms (II) and (III) in equilibrium, and that the high-melting form is a 1,4-diphenyl-5-thiolurazole, (I). This conclusion was reached for several reasons:

(1) In no case has the thiol methyl ester, (IV), corresponding to (I), been obtained from the pure low-melting acid, (II) or (III), in appreciable quantity. We have tested this point quantitatively and have never found more than 4 per cent. of this ester. The acid used by Marckwald,² which melted at 219°–221°, yielded a thiol methyl ester melting at 196°, and consequently was the form (I). Our own work amply confirms this conclusion. In every case the low-melting acid, (II) or (III), has, on esterification, given an oily product. This would be expected if it were the 1,4-diphenyl-5-thionurazole, which can exist in two forms, (II) and (III), and consequently would be likely to give a mixture of N-ester and O-ester, (V) and (VI).

In the presence of the phosgene the 2,4-diphenyl-3-thiosemicarbazide would function as a base and would react chiefly as



This should act with phosgene like all substituted ammonias and give first chiefly

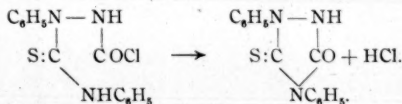


just as the phenylcarbazinic esters do when treated with

¹ After Dr. Nirdlinger's work was finished in June, 1909, and reported at the Detroit meeting of the American Chemical Society in July, 1909 (Slagle and Acree: *THIS JOURNAL*, **42**, 123), Professor Busch wrote me in the autumn of 1909 and stated later in *Ber. d. chem. Ges.*, **42**, 4763, that he now believes, on account of his recent work, his former views to be incorrect. He now advocates the formulas deduced from the work in the present communication as being correct.—S. F. A.

² *Ber. d. chem. Ges.*, **35**, 3098.

phosgene.¹ The group NHCOCCl could now, as an acid chloride, react with the weakly basic NHC_6H_5 group, giving the 5-thionurazole:



The mechanism of the reaction by which the methyl ester of the 2,4-diphenyl-3-thiosemicarbazide gives the urazole methyl thiol ester (IV) when treated with phosgene² is not sufficiently clear to warrant any assumptions regarding the reaction. There is no doubt, however, that the urazole ester has the structure (IV).

(2) The high melting acid (I) gives the corresponding methyl thiol ester (IV), as would be expected if it had the structure (I) and not the thion structure (II) or (III), formerly assigned to it by Busch.³ Busch's idea that the presence of the methyl thiol ester (IV) is due to a reverse rearrangement of the real thion acid, (II) or (III), on salt formation, is not in harmony with our data. For if the thionurazole rearranges into the thiolurazole in the presence of an alkylating agent and gives a corresponding thiol ester, it is hard to understand why the low-melting form, which Busch supposed to be the thiolurazole, always gives an oily mixture of ester, and never a thiol ester; if the thionurazole rearranges into the thiol acid and gives a thiol ester, the low-melting acid supposed by Busch to be a thiolurazole form should give this ester all the more readily.

(3) When the low-melting urazole, which when pure yields no thiol ester, is partially transformed, as indicated by a change in melting point, by heat or otherwise, into the high-melting acid, the resulting mixture yields on alkylation with alkalies and methyl iodide varying amounts of methyl thiol ester and less thion ester, depending upon the extent of the rearrangement.

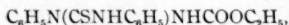
¹ Heinrichs: Diss., Erlangen, 1900.

² Marckwald: *loc. cit.*; Busch and Holzmann: Ber. d. chem. Ges., **34**, 340.

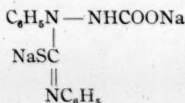
³ Ber. d. chem. Ges., **34**, 326.

(4) The work of Doctors Brunel, Johnson, Shadinger, Rogers and Nirdlinger shows that the salts of the 3-thiourazoles react with alkyl halides many times as rapidly as the corresponding 3-hydroxy salts, practically pure thiol esters being formed. Using this as a diagnosis, we are forced again to the conclusion that the high-melting urazole (225°) is the 5-thiol form, (I), and the low-melting form (141°) is the 5-thion compound, (II) or (III). The sodium salt of the high-melting urazole (225°) reacts, in alcoholic solutions of methyl iodide, about 80 times as rapidly as does the sodium salt of the low-melting form (141°). This is shown quantitatively on pages 239-242.

The only point not worked out yet is the fact that the carbethoxy ester,



gives the high-melting form on treatment with an alkali,¹ while it might give the low-melting acid. Unfortunately we have not been able recently to secure this ester again in order to saponify it *in the cold* with alkalies and learn whether the urazole acid formed is really a pure thiolurazole or a mixture of the two urazoles with the melting point of the thiolurazole, 225° (see p. 236). When we consider, however, the grouping $\text{R}(\text{CS})\text{NHC}_6\text{H}_5$, we see that in the presence of an alkali we could have part of the metal attached to the sulphur. The ester would be saponified and could give



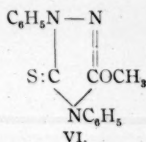
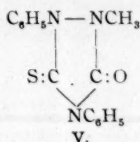
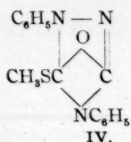
which could, on addition of an acid, split out water and change partly into the corresponding thiol acid, just as the methyl ester of the α -semicarbazide does when treated with phosphine.

In order to show that certain samples of these acids give their own separate esters we give the following as an exam-

¹ Grohman: Diss., Erlangen, 1900, p. 15.

ple: The sodium salt from 0.202 gram of the low-melting acid gave 0.2022 gram methyl ester which contained only 0.0088 gram of methyl thiol ester, while the sodium salt from 0.202 gram of the high-melting urazole acid gave 0.1843 gram of methyl ester which contained 0.1628 gram methyl thiol ester. This shows conclusively that this sample of low-melting acid gave practically no thiol ester, and that the high-melting acid gave practically all thiol ester. This is what we should expect if the low-melting acid is 1,4-diphenyl-5-thionurazole, (II) or (III), and the high-melting acid, 1,4-diphenyl-5-thiolurazole (I).

Knowing now the real constitution of these urazoles, let us consider what we should expect of them in the light of the theory of tautomeric salts. Firstly, we could expect each salt to give its own individual esters by a direct reaction. Then the pure sodium 1,4-diphenyl-5-thionurazole could, and does, give on alkylation with methyl iodide a mixture of the N- and O-esters, (V) and (VI), just as 1-phenyl-4-methylurazole yields the two corresponding N- and O-esters:



In solution, however, the sodium 1,4-diphenyl-5-thionurazole could, and does, rearrange slowly into sodium 1,4-diphenyl-5-thiolurazole, which gives the methyl ester (IV). This ester, which contains the SCH_3 group, should be, and is, very different from the two esters mentioned above, and can be separated quantitatively from them. Our problem then is to apply the proper equations to these reactions and determine whether we get constants as demanded by the theory. Whether we should use one equation or another depends on whether the rearrangement of the salts is reversible or not. Since it is not practicable to measure directly the ratio of the two salts in solution by conductivity or analogous methods, and

since the salts cannot be easily isolated from mixtures, the solution of the problem depends on the formation of stable derivatives from the two salts, the ratio of which can be measured. If we start with an individual salt, the problem would be to determine at any moment the ratio of thion to thiol ester formed. If, therefore, K and K_1 (see page 221) are much smaller than the reaction constants (K_2 and K_4) of any alkylating agent, it would be only necessary to determine K and K_1 independently by adding, for instance, a large excess of alkylating agent to a solution of the salt after any time period, and measuring the ratio of esters formed. In the same way, K_2 and K_4 could be determined independently by alkylating the pure salts under conditions such that there would be no appreciable rearrangement of these salts. In the case of these thiourazoles we have such conditions and this method can be used in all ordinary reactions of these compounds. Some alkylating agents, however, may be found, such that K , K_1 , K_2 and K_4 will have nearly equal values, when the integrals of the general equations given on page 222 can be used.

If accurate analytical methods can be developed for studying these tautomeric 5-thion- and 5-thiourazoles we shall take up at first the following problems:

- (1) The relative velocities of reaction of the two tautomeric forms with other compounds, in different solvents, at different temperatures, etc.
 - (2) The relative velocities of the rearrangement of each salt into the other, in water and other solvents, at different temperatures, and hence the value of the equilibrium constants; many salts, having various anions and various cations, will be used.
 - (3) Especially will attention be given to the question whether all these reactions are ionic or molecular or both. It is very important to know whether only the anions of the salts, or the undissociated salts, or more complex ions or double salts, or *all*, rearrange into each other, and whether in the different individual cases the anions, or the undissociated salts (or the cations and anions together), or more complex
- 

salts, or all together, may unite with the alkyl halides and form complex ions, or molecules, which can yield the end products.

All these questions are very complicated and can be solved only by a great amount of accurate work. Conclusions reached must be stated only tentatively and we are presenting our work and ideas only in this light. When our theory is no longer useful as a working hypothesis we shall throw it away.

EXPERIMENTAL.

2,4-Diphenyl-3-thiosemicarbazide.—This compound was made by the method of Busch and Holzmänn¹. To 10 grams of phenylhydrazine in 80 grams of alcohol, cooled in a mixture of salt and ice, 12.5 grams of phenyl mustard oil in 25 grams of cold alcohol were added. The semicarbazide separated out and after ten or fifteen minutes was filtered and washed with cold² alcohol. Twenty grams of pure compound melting completely at 139° were obtained.

1,4-Diphenyl-5-thionurazole was made by the method of Busch and Reinhardt.³ One hundred and twenty grams of a 20 per cent. solution of phosgene in toluene, cooled in a mixture of salt and ice, were added to 10 grams of 2,4-diphenyl-3-thiosemicarbazide suspended in 20 cc. of half-frozen benzene. The mixture was shaken thoroughly and allowed to stand in a salt and ice mixture for a few hours, and then at the laboratory temperature. At the end of 48 hours the solid was filtered off, dried on a clay plate and shaken out in a funnel with a liter of very dilute cold caustic potash solution. Then the solid (a) remaining was filtered off and the alkaline solution was cooled in ice and acidified with cold dilute hydrochloric acid. The precipitated urazole (b) was filtered off immediately; when the filtrate was kept in ice more of the urazole (c) separated. The precipitate (b) obtained above was dried, shaken out with cold dilute alkali and filtered and the solution acidified. In this way 5 grams of urazole

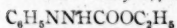
¹ Ber. d. chem. Ges., **34**, 324. Holzmänn: Diss., Erlangen, 1902.

² This substance rearranges into the isomeric 1,4-diphenyl-3-thiosemicarbazide when it is crystallized from hot alcohol, but Mr. E. P. Doetsch has found that it can be nicely purified, without rearrangement, by crystallization from hot benzene.

³ Reinhardt: Diss., p. 66.

were obtained; 2.5 grams from the second precipitation (b) and 2.5 grams from the filtrate (c). The substance melted completely when dipped into the melting-point bath heated to 141° , and then solidified and melted again at 220° – 222° . The substance obtained from the filtrate (c) was perfectly white and dissolved in alkalis, forming a colorless solution, while the urazole which was reprecipitated (b) was slightly brown in color and gave a yellowish solution. The per cent. of thionurazole in each sample can be determined only by an analysis. Some samples contain 90 per cent. thionurazole and others were over 99 per cent. pure.

1-Carboethoxy-2,4-diphenyl-3-thiosemicarbazide,



SC

NHC₆H₅

—An attempt was made to use this com-

pound for obtaining the 1,4-diphenyl-5-thiolurazole. The method of Busch and Grohmann¹ for making the semicarbazide was tried with no success. The following method gave good yields for a time: Twenty grams of 2,4-diphenyl-3-thiosemicarbazide were dissolved in 150 cc. of neutral chloroform in the presence of 25 grams of finely ground potassium carbonate and the mixture boiled under a return condenser. Then a slight excess of ethyl chlorcarbonate was added, and, after boiling one hour, half of the first amount of ethyl chlorcarbonate was added and the mixture boiled another hour. Then the chloroform solution was shaken out with water to remove the suspended potassium carbonate, dried, and the chloroform distilled off. An oil remained in the flask, which on standing deposited white crystals. Ether was added to the mixture, whereupon more crystals came out. They were filtered off and washed with ether; 7.5 grams of a substance melting at 143° – 144° were obtained. The melting point of the compound of Busch and Grohmann was 145° . This substance was obtained several times with equally good yields when suddenly it became impossible to obtain any of it at all. At least 20 experiments were tried under varying conditions

¹ Grohmann: Diss., Erlangen, 1900, p. 20.

and with different solvents but in no case was any of the compound ever obtained again. No apparent reason for this was found. This trouble caused considerable delay in the work, as the compound would have furnished the 1,4-diphenyl-5-thiolurazole easily, in any desired quantity.

1,4-Diphenyl-5-thiolurazole.—This was first made by the saponification of the above ester. It was suspended in a small amount of alcohol and a slight excess of a solution of sodium ethylate added. The crystals soon went into solution, water was added and the solution was acidified; a voluminous precipitate of 1,4-diphenyl-5-thiolurazole was then formed. The substance, when crystallized from alcohol, melted at 221° – 223° . After it was no longer possible to obtain the 1-carbethoxy-2,4-diphenyl-3-thiosemicarbazide, the thiolurazole was made by the rearrangement of the corresponding 1,4-diphenyl-5-thionurazole. For this purpose some of the 1,4-diphenyl-5-thionurazole was put into a test tube and dipped into a paraffin bath at 150° and kept there until it had fused and resolidified. Then it was dissolved in caustic potash and the solution filtered and precipitated with hydrochloric acid. The acid was filtered off and crystallized twice from alcohol. Then it was heated in a test tube to 160° for three hours in order to be certain that it was converted as completely as possible into the 1,4-diphenyl-5-thiolurazole. This was considered necessary, as a mixture of the two acids, containing about 50 per cent. of each, gives no sign of fusion when dipped into the melting point bath at 143° , and a mixture containing 80 per cent. of the 1,4-diphenyl-5-thionurazole barely shows signs of a fusion and resolidification wave traveling through the mixture at 143° . The substance was perfectly white and dissolved in alkalis, giving a colorless solution. It melted at 221° – 223° .¹ *The constancy of the melting point gives no clue regarding the relative percentages of the thiol- and the thionurazoles, and these experiments should be borne in mind in all work on tautomeric compounds. The ratio can be determined only by an analysis, as discussed later, and when we speak of the thiol- and thionurazoles we do not*

¹ Reinhardt: Diss., 1906.

mean that they are necessarily free from each other, unless it is definitely so stated.

Alkylation of 1,4-Diphenyl-5-thionurazole and 1,4-Diphenyl-5-thiolurazole with Diazomethane and -ethane.—In the earlier part of the work it was intended to study the rearrangement of the two acids by adding a diazoalkyl, and analyzing the mixture of esters obtained. On studying the action of diazomethane and -ethane on the two urazole acids, however, it was found that the esters obtained are different from those made from the sodium salts and methyl iodide. None of them split out methyl sulphydrate when heated with caustic potash, but they are decomposed, and give off hydrogen sulphide when the mixture is acidified.

Two grams of 1,4-diphenyl-5-thionurazole were suspended in ether and an ethereal solution of diazomethane was added until the yellow color of the diazomethane persisted. Then the ether was evaporated off. An oil remained which solidified on standing a week in a vacuum desiccator. The solid, after being washed twice with cold alcohol, melted at 74° .5– 75° .5. Analysis showed that it had the composition $C_{15}H_{13}ON_3S$. Yield, 1.2 grams. From 0.1210 gram of the ester heated 5 minutes at 90° , with a 3 per cent. solution of alcoholic potash, 0.015 gram of unchanged substance was obtained. Several other similar experiments were tried under different conditions of temperature, but with results of the same nature. One gram of 1,4-diphenyl-5-thionurazole under the same conditions gave, with diazoethane, an oil from which, on solidification and crystallization from alcohol, an ester melting at 79° – 81° was obtained. Yield, 0.5 gram. The analysis showed it to have the composition $C_{16}H_{15}ON_3S$.

Two grams of 1,4-diphenyl-5-thiolurazole, when treated with diazomethane, gave an ester which, when crystallized twice from alcohol, melted at 129° .5– 130° .5 (uncor.). Analysis showed it to be isomeric with the ester obtained from 1,4-diphenyl-5-thionurazole and diazomethane: 0.1847 gram of this ester when heated one hour at 100° with 5 cc. of a 10 per cent. alcoholic solution of potassium hydroxide, gave back 0.0215 gram of unchanged ester. In another case, 0.0315

gram unchanged substance was obtained from 0.0864 gram ester on heating it 15 minutes at 100° with 5 cc. of 3 per cent. caustic potash. Results of a like character were obtained in experiments at 50°. 1,4-Diphenyl-5-thiolurazole and diazomethane gave an ester which, when crystallized from ligroin, melted at 105°.5–107°.5. The fact that diazomethane does not give the 5-thiolurazole methyl ester melting at 196° is strong proof, with other such cases, that the diazoalkyls cannot be *absolutely* depended upon to give derivatives corresponding to the mother substance.

Owing to the fact that neither of the compounds obtained by treating the two acids with diazomethane reacted in a definite way with caustic potash it was impossible to separate the two, and consequently this phase of the work had to be abandoned. We shall later take up these reactions exhaustively. On account of the fact that diazomethane forms ring compounds with unsaturated substances, which double compounds may decompose further in some cases, it may be difficult to trace the relation between the constitution of the ester and that of the acid from which the ester is obtained.

Preliminary Experiments on the Alkylation of Sodium 1,4-Diphenyl-5-thionurazole and Sodium 1,4-Diphenyl-5-thiolurazole.—No attempt was made to isolate the sodium salts of the two acids, but in all cases the weighed amount of acid was titrated with the corresponding amount of sodium hydroxide. That this procedure can be used is shown by the following figures:

0.3983 gram of 1,4-diphenyl-5-thionurazole required 29.50 cc. 0.05 N NaOH. The calculated amount is 29.60 cc.

0.4050 gram of 1,4-diphenyl-5-thiolurazole required 30.20 cc. 0.05 N NaOH. The calculated amount is 30.08 cc.

Owing to the fact that Reinhardt¹ was unable to obtain the esters of the two acids from the sodium salts and methyl iodide the conditions governing the preliminary experiments were carefully watched. It was soon found, however, that at 50° or 60° or even at lower temperatures, large yields of

¹ *Loc. cit.*

the esters of the two acids can easily be obtained in a short time. It was simply necessary to add an alcoholic solution of methyl iodide to an aqueous solution of the sodium salt, and to heat this at 50° or 60° for an hour or two. Later when 20 molecules of methyl iodide (always in alcohol) were used, nearly quantitative yields of ester were obtained from each of the acids in 20 minutes.

The velocity of alkylation of the two salts with methyl iodide was first studied in order to obtain their relative reactivities. The procedure was as follows:¹

1,4-Diphenyl-5-thionurazole (0.4039 gram) was weighed in a tube sealed off at one end and 3 cc. 0.5 N NaOH were run in from a burette. After the acid had dissolved, 2 cc. of 0.75 N solution of methyl iodide in ethyl alcohol were added, the tube sealed off, and put in the constant temperature bath and shaken. At the end of the time period t , it was taken out, cooled in ice water and opened, and the contents poured into an extraction funnel containing very dilute alkali. The ester² was extracted by shaking out the solution 6 times with chloroform. The chloroform was evaporated off below its boiling point in a weighed porcelain dish and the ester dried to constant weight, x , in a vacuum desiccator. The results of these quantitative experiments are given in Table I below.

That the extraction removes nearly all of the ester from the solution is shown by the following figures:

After 0.2955 gram methyl 1,4-diphenyl-5-thionurazole ester was extracted 6 times with dilute caustic potash, 0.2922 gram, or 98.87 per cent., was removed.

From 0.2949 gram methyl 1,4-diphenyl-5-thiolurazole, treated as above, 0.2920 gram ester, or 99 per cent., was recovered.

¹ Ber. d. chem. Ges., **41**, 3199.

² We have shown that this ester is a mixture of two thion esters—a N-ester [(V), page 233], and an O-ester [(VI), page 233]. We have not determined the ratios of these two esters, but this problem has been studied by Mr. E. P. Doetsch. The fact that this thion salt may be an equilibrium mixture of the $=N-Na$ and $-N=C(ONa)$ salt does not change the relations presented in this article.

Table I.—0.3 Wt. N Sodium Salt of 1,4-Diphenyl-5-thionurazole and 0.3 Vol. N Methyl Iodide in Ethyl Alcohol at 50°.

t (minutes).	A.	x.	A - x.	AK.
30	0.4249	0.1103	0.3146	0.0117
60	0.4249	0.1705	0.2544	0.0112
180	0.4249	0.2882	0.1367	0.0117
240	0.4249	0.3071	0.1178	0.0109

Average, 0.0114

The ester obtained was a viscous reddish oil, which, on standing, became semisolid.

The sodium 1,4-diphenyl-5-thiolurazole is so reactive with methyl iodide that no constants could be obtained at 50°. For example, 3 cc. 0.5 N sodium 1,4-diphenyl-5-thiolurazole and 2 cc. 0.75 vol. normal methyl iodide, at 50°, gave, in two hours, 0.3511 gram ester. In 5 minutes, at 25°, over 0.3 gram ester was obtained. In 15 minutes, at 60°, under the same conditions, 0.3584 gram ester was obtained, while in 4 hours only 0.3358 gram was found. This shows that practically all the ester is formed in a few minutes, and that it then slowly decomposes. This is also shown by the fact that on opening the tubes there was a strong odor of methyl mercaptan. The ester obtained was perfectly white and after one crystallization from alcohol and drying on the water bath melted sharply at 196°–197° to a clear, colorless liquid. It was identical with the ester obtained by treating 2,4-diphenyl-3-methylthiosemicarbazide with phosgene; a mixture of the two samples melted at 196°.

Since the thiol salt reacts so rapidly with methyl iodide at 25° or 50°, it was evident that the study of the reaction velocity must be done at 0°. The following table shows the data obtained in 50 per cent. alcohol by Mr. E. P. Doetsch.

If we assume a temperature coefficient of 2 for an increase of 10° AK would be 0.1344 at 50°. This means, when differences in concentration are considered, that the sodium thiol salt reacts about 80 times as rapidly with methyl iodide as does the sodium salt of 1,4-diphenyl-5-thionurazole.

Table II.—0.045 N Sodium Salt of 1,4-Diphenyl-5-thiolurazole and 0.045 N Methyl Iodide at 0°.

<i>t</i> (minutes).	A.	x.	A - x.	AK.
30	0.2394	0.0327	0.2067	0.00527
30	0.2394	0.0298	0.2096	0.00473
60	0.2394	0.0457	0.1937	0.00393
120	0.2394	0.0712	0.1682	0.00353
240	0.2394	0.1160	0.1234	0.00391
360	0.2394	0.1396	0.0998	0.00388
990	0.2394	0.2018	0.0376	[0.00540]
1265	0.2394	0.2097	0.0297	[0.00552]

Average AK = 0.0042

When the tubes were opened only a faint odor of mercaptan was observable, a proof that the thiol ester is hardly hydrolyzed at 0°.

Hydrolysis and Separation of the Esters.—Owing to the easy decomposition of the 1,4-diphenyl-5-methylthiolurazole by caustic potash into methyl mercaptan and potassium 1,4-diphenylurazole, it was at the beginning recognized that this would be the easiest way to separate this ester from a mixture containing it and the methyl esters of 1,4-diphenyl-5-thionurazole.

It was not so easy, however, to find an experimental method to hydrolyze this ester quantitatively, and at the same time not appreciably decompose the esters of the 1,4-diphenyl-5-thionurazole. In the preliminary experiments with 1,4-diphenyl-5-thiolurazole, a weighed amount of ester and enough alcohol to dissolve the ester was put in a porcelain dish on the water bath, and then various amounts of alkali were added. This method is easier than that involving the sealed tubes which we have used several years, although not so accurate. After a certain time the contents of the dish were washed into a funnel and the unhydrolyzed substance extracted with chloroform. Then the solution was acidified and the precipitated 1,4-diphenylurazole was extracted with chloroform and weighed as a check. The following results were obtained:

Weight of ester.	Amount of alkali.	Time heated (minutes).	Amount not hydrolyzed.	Per cent.	Per cent. of 1,4-diphenyl urazole recovered.
0.1995	10 cc. 0.25 N	20	0.0007	0.35	93.0
0.2047	10 cc. 0.50 N	20			92.2
0.1546	20 cc. 0.50 N	15	0.0004	0.25	96.0

This shows conclusively that the 1,4-diphenyl-5-methylthiolurazole can be hydrolyzed practically quantitatively. But when the oily esters of 1,4-diphenyl-5-thionurazole were treated by the above method they were not only badly decomposed, but the oil floated on top of the alkali and crept over the side of the dish. On this account the experiments in open dishes were abandoned. Then the methyl thiol ester was heated at 60° in sealed tubes with various amounts of alkali the tubes being shaken during the hydrolysis.

Weight of ester.	Amount of alkali.	Time of hydrolysis.	Amount not hydrolyzed (grams).	Per cent.
0.1460	10 cc. 0.25 N KOH	16 hrs.	0.0004	0.28
0.1017	10 cc. 0.10 N KOH	35 min.	0.0015	1.4

In the actual experiments, however, it is necessary to use chloroform in transferring the esters from the dishes in which they were weighed. The greater part of the chloroform is evaporated off, but one or two cc. always remain with the ester, and this is generally eliminated by repeated evaporation with small quantities of pure ether. Nirdlinger then introduced the "Künstgriff" of testing whether the methyl thiol ester could be hydrolyzed in the presence of chloroform in the tubes at 60°.

In the following experiment a weighed amount of 1,4-diphenyl-5-methylthiolurazole was put into tubes sealed off at one end and then 2 cc. chloroform and a certain amount of alkali were added. The tubes were sealed off at the other end and heated at 60°:

Weight of ester.	Amount of alkali.	Time of hydrolysis.	Amount not hydrolyzed (grams).	Per cent.
0.0835	10 cc. 0.1 N KOH	1 hour	0.0006	0.72

Then the methyl thion esters were treated in the same way.

These esters were obtained by alkylating sodium 1,4-diphenyl-5-thionurazole and extracting the ester with chloroform as explained before. After the ester had come to constant weight in the dish it was transferred to the small tubes drawn out to a capillary at one end, and the chloroform evaporated down to 1 or 2 cc. Then the tube was constricted at the other end, the alkali added and the tube sealed off. The tubes were heated at 60° with constant shaking:

	Weight of ester.	Amount of alkali.	Time of hydrolysis (hours).	Amount not hydrolyzed (grams).	Per cent. not hydrolyzed.
1	0.2477	10 cc. 0.1 N KOH	1	0.2385	96.2
2	0.2950	10 cc. 0.1 N KOH	1	0.2883	97.7
3	0.1724	10 cc. 0.1 N KOH	1	0.1684	97.6
4	0.1684	10 cc. 0.1 N KOH	1	0.1674	99.4

In experiments 1, 2 and 3 the ester was taken in the condition in which it was obtained from the action of methyl iodide and sodium 1,4-diphenyl-5-thionurazole. We should expect some loss here due to the formation of the methyl thiol ester from that part of the salt which rearranged into the other form during the alkylation, and from some of the thiol salt present originally. Experiment 4 is of especial importance, as in this case the ester remaining after hydrolysis in experiment 3 was used. This is the real test of our method and we see that in the presence of the chloroform the methyl esters of 1,4-diphenyl-5-thionurazole are not appreciably attacked by dilute caustic potash at 60°.

Then experiments were tried with mixtures of the methyl esters. The procedure was that used above, the methyl thiol ester being weighed into the tubes before the other ester had been washed in by means of chloroform:

Thiol ester.	Thion ester.	Alkali.	Weight of unhydrolyzed ester.	Time.
0.0623	0.2278	8 cc. 0.25 N KOH	0.2291	2
0.0510	0.2258	8 cc. 0.25 N KOH	0.2255	2

By this procedure, then, the esters are separated quantitatively, the methyl thiol ester being hydrolyzed and giving methyl sulphhydrate and 1,4-diphenylurazole, while the oily methyl esters of 1,4-diphenyl-5-thionurazole remain in the

chloroform and are not greatly affected by the alkali. The 1,4-diphenylurazole can be recovered to the extent of about 95 per cent. by acidifying the aqueous solution in the funnel, and extracting with chloroform.

It was at once realized that if the esters were to be used as a means of analyzing the mixture of salts at any moment a method must be devised for alkylating the salts quantitatively in a short time and giving a ratio of esters corresponding to the ratios of the two salts. Since other researches in the urazole group have shown that the ratio of esters may change with the change in solvent we decided to try first a mixture of water and alcohol. Mr. E. P. Doetsch has since learned that the presence of the alcohol has a serious disturbing effect on the apparent ratios of the salts, and that the hydrolysis of the thiol ester during the alkylation must be suppressed by making the solution *neutral* by adding a mixture of mono- and disodium phosphates or other similar compounds. The results of the present investigation must therefore be considered as preliminary.

After various experiments it was found that 20 molecular equivalents of methyl iodide and either salt, in about 7 cc. of 60 per cent. alcohol, will give practically quantitative yields of ester, at 60°, in from 15 to 20 minutes. From 0.404 gram 1,4-diphenyl-5-thionurazole, 0.417 gram methyl ester was obtained. The theoretical amount is 0.425 gram. Furthermore, 0.404 gram of 1,4-diphenyl-5-thiolurazole gave 0.409 gram ester under the same conditions. Then the two salts (0.2 gram) were alkylated and the esters analyzed in order to determine the purity of the acids used:

1,4-Diphenyl-5-thionurazole.

	Weight of ester.	Weight of ester after hydrolysis.	Loss.	Per cent purity of acid.
1	0.2022	0.1934	0.0088	95.65
2	0.1976	0.1914	0.0062	96.86

1,4-Diphenyl-5-thiolurazole.

1	0.1690	0.0198	0.1492	88.29
2	0.1843	0.0215	0.1628	88.34
3	0.1818	0.0195	0.1623	89.3
4	0.1843	0.0187	0.1656	89.86

It is seen in this last table that the alkylations were not complete. As a final check on the method, known weights of the two acids were mixed, the theoretical amount of sodium hydroxide added and the salts alkylated. Then the esters were analyzed. In calculating the actual amount of each acid in the mixture the 1,4-diphenyl-5-thionurazole was taken as being 96.25 per cent. pure, and the 1,4-diphenyl-5-thiolurazole as being 89 per cent. pure:

Weight of 1,4-diphenyl-5-thionurazole (1) (gram).	Weight of 1,4-diphenyl-5-thiolurazole (2) (gram).	Calculated per cent. of (1) in total acid.	Found.
0.1020	0.100	53.9	55.6
0.0455	0.1565	30.5	31.7
0.1465	0.0555	72.6	71.5
0.1000	0.1020	52.9	53.5
0.1500	0.0520	74.2	73.6

The check experiments described in this section show that the method, taken as a whole, is accurate to well within 5 per cent. A more systematic study of the time and the concentration of alkali necessary for complete hydrolysis of the methyl thiol ester, and the conditions for complete alkylation of the salts, would without doubt reduce the maximum error to 2 or 3 per cent. The results of the rearrangement experiments described below appear, on the surface, to be very satisfactory. Such, however, is not the case and this fact must serve as a warning against the hasty acceptance of mere mathematical concordance of the results. In this physical-organic research there are so many uncertainties until each problem is studied deeply that the conclusions can be only tentative.

Rearrangement Experiments.—While the method of analysis of the salt mixtures was being worked out, preliminary experiments were made on the rearrangement of sodium 1,4-diphenyl-5-thionurazole. The first experiments were carried out at 100°. Three cc. of a 0.5 weight N solution of sodium 1,4-diphenyl-5-thionurazole were sealed in a small tube holding about 6 cc. and the tube was fastened in the neck of a flask half full of rapidly boiling water. After certain intervals the tubes were opened and 2 cc. of 0.75 vol. N methyl iodide

in ethyl alcohol¹ were run in and the tubes were sealed up again. This made the whole solution approximately 0.3 N. After heating two hours at 60° the contents of the tubes were poured into extraction funnels and the esters were extracted with chloroform and weighed. In one experiment lasting twenty-two hours, practically pure methyl ester of 1,4-diphenyl-5-thiolurazole was obtained on alkylation, so no further work was done at 100°. Then tubes were heated in the same way at 60° and alkylated. After heating one tube eleven hours and then alkylating, 0.201 gram of ester was obtained which contained 80 per cent. of the esters of 1,4-diphenyl-5-thionurazole. Although only about half of the salt had been alkylated, this indicated very well that the reaction could be studied at 60°.

Meanwhile the method for the analysis of the mixture of salts had been worked out, so the procedure finally adopted was as follows: 0.202 gram of 1,4-diphenyl-5-thionurazole was weighed into a tube holding about 8 or 9 cc. and the tube was drawn out to a long capillary at the open end. Then 1.5 cc. of 0.5 N sodium hydroxide and 1.5 cc. of water were run in and the tubes sealed off. This made the solution 0.25 weight N with respect to the salt. The tubes were put into a bath² kept at 60° for certain time periods and then taken out. The very tip of the capillary was broken off and 4 cc. of 3.75 vol. N methyl iodide were run in, the capillary was sealed up again and the tube then put back into the bath. At the end of twenty minutes it was taken out, opened, and the contents were poured into a separating funnel containing water to which a few drops of alkali had been added. The ester was extracted with 6 portions (5 cc. each) of chloroform, the chloroform was evaporated off in a weighed porcelain dish, and the ester was then dried to constant weight at 55° in an air bath. The ester was transferred by means of chloroform to small tubes, drawn off to a capillary at the lower end, and

¹ As stated above, the alcohol should not be used. Mr. E. P. Doetsch has shown that when the alcohol is present there is a more rapid change of the ratio of the salts during the alkylation than when water alone is used. While our results are fairly concordant, they are only tentative.

² For a description of the bath used see Brunel and Acree: *THIS JOURNAL*, **43**, 533.

the solvent was evaporated down to about 2 cc. by dipping the capillary part of the tube into a water bath at 80°. *To prevent bumping a capillary stirring rod is inserted well down into the capillary end of the tube.* Then 5 or 6 cc. of half-normal potassium hydroxide were added and the tubes sealed off. They were shaken for two hours in the 60° bath, and opened, and the unhydrolyzed ester extracted in the usual way. The following table shows the results obtained in a large number of experiments:

Table III.

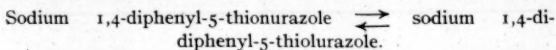
Time (hours).	Weight of total ester.	Weight of unhydrolyzed ester.	Per cent. thion ester (C—C ₂).
0	0.1976	0.1914	96.8
	0.2022	0.1934	95.7
6	0.1987	0.1775	89.3
	0.2010	0.1800	89.5
12	0.2058	0.1652	80.3
	0.2037	0.1625	79.8
18	0.2110	0.1565	74.2
24	0.2007	0.1410	70.4
36	0.1977	0.1374	69.7
	0.1705	0.1083	63.5
	0.1945	0.1230	63.2
42	0.2013	0.1192	59.2
96	0.1726	0.0556	32.3
	0.1618	0.0516	31.9
168	0.1584	0.0384	24.2
216	0.1732	0.0343	19.8
	0.1686	0.0319	18.9
336	0.2019	0.0204	10.1

Experiments were carried out in the same way with sodium 1,4-diphenyl-5-thiolurazole.

Table IV.

Time (hours).	Weight of total ester.	Weight of unhydrolyzed ester.	Per cent. thion ester (C—C ₂).
0	0.1690	0.0198	11.7
0	0.1843	0.0215	11.7
0	0.1818	0.0195	10.7
0	0.1843	0.0187	10.1
48	0.1868	0.0214	11.5
120	0.1760	0.0280	15.9
	0.1805	0.0295	16.3

These figures show that the reaction is slightly reversible and that we have:



If the reaction is monomolecular¹ then

$$(1) \frac{dc_2}{dt} = K_1(C - C_2) - K_2(C_1 + C_2),$$

where C is the original concentration of the sodium 1,4-diphenyl-5-thionurazole, C_1 that of the sodium 1,4-diphenyl-5-thiolurazole present at first, and C_2 that of the rearranged salt.

At equilibrium,

$$\frac{K_1}{K_2} = \frac{C_1 + C_2}{C - C_2}$$

Substituting $\frac{K_1}{K_2} = K$ in equation (1) and integrating we get

$$\frac{1}{t} \log \frac{KC - C_1}{KC - C_1 - (K + 1)C_2} = K_1 + K_2.$$

Since in a unimolecular reaction the unit of concentration is immaterial we can assume that C is 96.25 and C_1 is 3.75. The experiments given above do not give the definite equilibrium ratio but the most probable one is the value for sodium 1,4-diphenyl-5-thionurazole heated for 336 hours, where C_2 is equal to 96.25-10.1, or 86.15. Then,

$$K = \frac{K_1}{K_2} = \frac{3.75 + 86.15}{96.25 - 86.15} = 8.9$$

Table V.

$T.$	$C.$	$C_1.$	$C_2.$	$K_1 + K_2.$	$K_1.$	$K_2.$
6	96.25	3.75	6.9	0.0061	0.0055	0.00061
12	96.25	3.75	16.3	(0.0076)	(0.0068)	(0.00076)
18	96.25	3.75	22.1	0.0071	0.0064	0.00071
24	96.25	3.75	26.3	0.0066	0.0059	0.00066
36	96.25	3.75	33.0	0.0058	0.0052	0.00058
42	96.25	3.75	37.1	0.0060	0.0054	0.00060
96	96.25	3.75	64.2	0.0062	0.0056	0.00062
168	96.25	3.75	72.3	(0.0047)	(0.0042)	(0.00047)
216	96.25	3.75	76.9	(0.0045)	(0.0041)	(0.00044)

¹ In the equations no account is taken of the question whether the molecules or the ions of the salts undergo transformation. In either case it would merely be necessary to substitute for c and c_1 the values ac or $(1-a)c$, and $a'c_1$ or $(1-a')c_1$ and hence introduce new constants. According to the isohydric principle a and a' should be practically constant during the reaction. It is also not greatly material whether c or c_1 represents a mixture of two salts in nearly instantaneous equilibrium.

This series, while only preliminary, shows apparently that the reaction is monomolecular and especially that the salts rearrange into each other. It is especially to be regretted that in many of the experiments in the above tables the weight of ester is much below the theoretical. As stated above, however, Mr. E. P. Doetsch has obtained better results where no alcohol is present.

Conclusions.

1. It has been shown that the compound supposed by others to be 1,4-diphenyl-5-thiolurazole is in reality 1,4-diphenyl-5-thionurazole, and that the one supposed by them to be 1,4-diphenyl-5-thionurazole is 1,4-diphenyl-5-thiolurazole.

2. This work shows that we can convert these two acids into salts which have two different tautomeric forms, one corresponding to the structure of 1,4-diphenyl-5-thionurazole and the other corresponding to the structure of 1,4-diphenyl-5-thiolurazole. These two salts not only give back their corresponding acids on the addition of hydrochloric acid, but they also give their own characteristic derivatives. The silver salts of the two acids are also different. The two sodium salts have each been alkylated with equivalent amounts of methyl iodide. The sodium 1,4-diphenyl-5-thionurazole and methyl iodide in 0.3 N solution (40 per cent. alcohol) at 50° give a very good constant, $AK = 0.0114$, only about 75 per cent. of the salt being alkylated in 4 hours at 50°. The sodium 1,4-diphenyl-5-thiolurazole is alkylated 75 per cent. in 5 minutes at 25°, while this salt and methyl iodide in 0.045 N solution (50 per cent. alcohol) at 0° give the constant $AK = 0.0042$. If we assume a temperature coefficient of 2 for each 10° and take into consideration differences in concentration, the experiments show that methyl iodide reacts about 80 times as rapidly with the sodium salt of 1,4-diphenyl-5-thiolurazole as it does with the other sodium salt, and this fact gives further evidence that we have assigned the correct structure to the higher-melting form.

3. The sodium salts of these two acids have been esterified

quantitatively and a method, accurate to within 5 per cent., has been devised for analyzing a mixture to the two salts. A mixture of the esters can be analyzed accurately with an error of 2 or 3 per cent.

4. It is shown further that the sodium salts are mutually convertible into each other through two apparently reversible unimolecular reactions, and that the velocity of rearrangement of the sodium 1,4-diphenyl-5-thionurazole is approximately 9 times as large as that of sodium 1,4-diphenyl-5-thiolurazole. The thiol salt is less reactive in this reversible change but much more reactive in the alkylation experiments. A study of the relationship of the energy changes involved in the two reactions is of the greatest importance.

5. Work with these compounds should throw great light on tautomerism. We can actually isolate the tautomeric acids and their corresponding salts, and can study accurately many of the tautomeric phenomena exhibited by these substances. Other types of tautomeric compounds, such as acetacetic ester, cyanides, cyanates, nitrophenols, phenolphthaleins, oximes, amidines, and many others, whose properties do not so readily admit of such quantitative study, exhibit many of the tautomeric phenomena belonging to the urazoles. It is therefore possible that further work on these urazoles will help us to understand more about the large number of classes of substances known under the name of tautomeric compounds.

JOHNS HOPKINS UNIVERSITY.
BALTIMORE, June 1, 1909.

THE DIFFUSION OF CRUDE PETROLEUM THROUGH FULLER'S EARTH.

BY J. ELLIOTT GILPIN AND OSCAR E. BRANSEY.¹

INTRODUCTION.²

It is a well-established fact that the petroleum obtained from the sandstones of the Upper Devonian and Mississippian

¹ Dissertation submitted to the Johns Hopkins University by Oscar E. Branseý for the degree of Doctor of Philosophy.

² This research was aided by a grant received from the C. M. Warren Committee of the American Academy of Arts and Sciences.

periods, generally known as the Pennsylvania oil, differs markedly from the natural oil found in the Trenton limestone, usually designated as the Ohio oil, or Trenton limestone oil. Both of these oils, in turn, are distinctly different from the petroleum occurring in the loose sands and soft shales of California. The unconsolidated tertiary clays, sands, and gravels in the southern United States, particularly in Texas, yield another variety of petroleum, characterized by properties more or less different from any of the preceding oils.

Not only do these differences exist between oils found in separate regions, but extreme variations in color and specific gravity, as well as in chemical composition, often occur between those of neighboring localities. On the other hand, close resemblances abundantly occur between petroleum of sections widely removed from each other. Some of the South American and many of the European oils, for instance, have been found to possess properties very similar to those of the oils of the southern United States; while the oil from the Corniferous limestone of Canada closely resembles the Ohio petroleum.

These variations in the oils of the United States and other countries have been carefully studied by many investigators. Such noted workers as Warren, Storer, Mabery, Pelouze, Cahours, Schorlemmer, Beilstein, Markownikoff, Engler, and Kurbatoff have devoted their lives to this subject. The question that naturally arises in connection with these variations is: Are these differences fundamental? Is the Pennsylvania petroleum as distinctly different from the Ohio oil as one chemical compound is from another? In answer to these questions, the following extract from a paper read by Mabery¹ in 1903 before the American Philosophical Society is of considerable importance: "Now, after years of arduous labor, I have reached the conclusion that petroleum from whatever source is one and the same substance, capable of a simple definition—a mixture of variable proportions of a few series of hydrocarbons, the product of any particular field differing from that of any other only in the proportion of the series and the members of the series." The evidence supporting

¹ P. Am. Phil. Soc., 1903.

this declaration has been, and is accumulating constantly, and, at the present time, this view is generally accepted.

If petroleum, then, is one and the same substance, how can the extreme variations between the American oils be explained? Were the causes operating in the formation of the Pennsylvania oil, almost barren of sulphur and nitrogenous bodies, different from those acting in the production of the sulphur-bearing oils of Ohio, or the heavy sulphur and nitrogenous oils of California?

To account for the formation of crude petroleum, two views, as is well known, the organic and inorganic, have been advanced. The Pennsylvania oil, according to these theories, may have been formed either from organic or inorganic substances, or from both. It is as yet impossible, however, to state conclusively from which of these sources the oil was derived. It is apparent, therefore, that the differences between the Pennsylvania and the Ohio, Texas, and California oils cannot be explained upon the assumption that the former was formed from organic remains, while the latter were produced from inorganic matter, or *vice versa*. If, however, crude petroleum is organic in origin, it may have been formed either from vegetable or from animal remains. The following discussion is based upon the assumption that the above-mentioned oils were derived from an organic source.

It has been suggested that the differences between these oils may be accounted for by assigning a vegetable origin to the Pennsylvania oil, and an animal origin to the others. Mabery¹ states that "It would seem that the small proportion of these bodies² in the Pennsylvania oil, as compared with the larger proportions in the limestone oils and California oils should be strong evidence in favor of a different origin, that the Pennsylvania oil came from organic vegetable remains, which should permit of the small amounts of sulphur and nitrogen compounds from this class of oils." Newberry, Peckham, Orton, and other geologists also favor the view that the Pennsylvania oil is of vegetable origin, and is derived

¹ P. Am. Phil. Soc., 1903:

² Reference is made to the sulphur, nitrogen, and oxygen compounds in petroleum.

from the organic matter of the bituminous shales of the Devonian period.

The facts which have led to the association of this oil with a vegetable source are, first, that the oil is of a different character from the limestone oils of Ohio, and those of Texas and California; second, that the Pennsylvania petroleum is found in strata that bear but few fossils; third, the belief that the Chemung and immediately overlying formations are barren of animal organic remains; fourth, the existence of large quantities of microscopic fossils, whose origin many believe to be vegetable, in the black shales of the Lower and Middle Devonian periods, to which formations many investigators are inclined to refer the origin of the Pennsylvania oil.

It is generally recognized that the Pennsylvania oil differs markedly from the Ohio, Texas, and California oils. Investigation has shown that the former contains a much larger proportion of the paraffin hydrocarbons, and a much smaller percentage of benzene and unsaturated hydrocarbons and sulphur and nitrogenous bodies, than the latter oils. It is further generally admitted that the Pennsylvania oil was not formed *in situ*. These two facts have aided strongly in assigning a vegetable origin to this oil. To what strata, then, should the source of the oil be referred? The great coal formations of Pennsylvania, lying above the Chemung, seem, at a first glance, to offer a solution of this problem. It is a notable fact, however, that these formations have not, up to the present time, been connected, either chemically or geologically, with the Pennsylvania oil. The possibility exists, however, that it was formed from vegetable remains in the Carboniferous formations above, and that then, by downward diffusion, it reached its present position in the Chemung. This view rests upon the physical fact that a liquid diffuses by the force of capillarity in all directions, downward as well as upward. Little attention has been given to this possibility, but it seems to deserve a very careful study. Owing, however, to the universal association of water under hydrostatic pressure with natural oil and gas, the migration of the latter is generally upward. This fact is attested by the accumulation of oil

in anticlinal folds when water is present, and by the existence of the remarkable gushing oil wells. That the Pennsylvania oil, if not formed *in situ*, ascended to its present location seems, therefore, more probable.

In what strata below the Chemung, then, was the oil originally produced? It has been previously mentioned that a number of investigators refer the source of the oil to the black shales of the Lower and Middle Devonian periods. The organic matter of these shales is composed largely of microscopic sporangites, which suggest the existence, according to Orton, of masses of floating vegetation, or Sargasso seas. According to this view, the origin of the Pennsylvania oil is vegetable in character, and its primitive abode was in the shales of the Devonian age lying below the Chemung sandstone, to which it ascended under the influence of natural agencies. Another origin, animal in character, may be assigned to this oil. This view is that the oil was formed in the fossil-bearing strata of the Chemung age, and that it diffused to the sandstone reservoirs in which it is now found, and that during such a diffusion its original character was changed. Prof. C. K. Swartz, of the Johns Hopkins University, who has made a critical study of the Chemung strata in Maryland, informs us that fossil remains exist in considerable abundance in the strata of this age in Maryland and adjoining areas. In Pennsylvania, the corresponding strata have been found to bear many fossils. It is possible that the oil formed in these strata, and then diffused to the strata in which it now exists and which are barren of fossil remains.

The evidence accumulated in this investigation seems to show that it is not necessary to assign a vegetable origin to the Pennsylvania oil to explain the differences between it and the oils of Ohio and California. It is clear from the results of this and other investigations that, when such oils as those of Ohio and California and Texas, which seem to be of animal origin, are allowed to diffuse through such porous media as fuller's earth, they yield oils very similar to those of Pennsylvania. By assuming, therefore, that the Pennsylvania oil migrated from some primitive source, in which it may

have been formed from animal remains, through shales, limestones, and sandstones, its peculiar character can be understood.

Whatever the original home of the oil, it seems probable that it migrated to its present location from some place below. It is with the changes occurring in crude petroleum as a result of such a migration through porous strata that the present investigation is primarily concerned.

In 1897, Dr. David T. Day,¹ from his own observations, and those of Dr. John N. MacGonigle, proposed the view that the Pennsylvania oil, at some past time, possessed properties very similar to those of the Ohio oil, but that in its migration to its present abode from regions below, its character was changed to its present condition.

Guided by this view, he conducted, in the laboratories of the United States Geological Survey, an investigation into the changes occurring in crude petroleum when allowed to diffuse through porous media, such as fuller's earth. He demonstrated clearly that an oil resembling the light Pennsylvania oil could be readily produced in the laboratory from the heavier crude Ohio oil. Glass tubes were packed firmly with the dry earth, through which the crude oil diffused by its own force of capillarity. From the earth of the upper sections of the tubes, very light, in some cases colorless, oils were liberated by treatment with water; from the earth of the lower sections of the tubes, much darker and heavier oils were obtained.

It will be observed that the fractionation is effected entirely by capillarity; oils with different surface tensions rise with different velocities through the capillary openings, such as the fine interstices and minute pores of the fuller's earth. A separation of the various constituents making up the complex of any one oil is thus produced. The view once held that this phenomenon is chemical was clearly disproved by Engler and Albrecht² in 1901, and later by other investigators.

¹ P. Am. Phil. Soc., 1897.

² Z. angew. Chem., 1901, 889.

Any medium, therefore, sufficiently fine-grained and porous to afford capillary spaces causes a separation of the constituents of any mixture, provided they possess different surface tensions. The compact sandstones, shales, and limestones that recur in many cycles throughout the earth's crust present an excellent medium for the separation of the constituents of such a complex mixture as petroleum. The force of capillarity, assisted by the hydrostatic pressure of the water occurring in the interior of the earth, acting over vast periods of time, is, it seems safe to state, sufficiently powerful to transport the oil from the lower regions to those above. That the conditions, therefore, to cause such a migration, with the consequent fractionation of the original oil, are abundantly present, appears extremely probable.

Let us examine, now, the conduct of the constituents of petroleum subjected to such a fractionation. The members composing the natural oil may be grouped under the following general heads: paraffin, aromatic, unsaturated hydrocarbons, sulphur, nitrogen, and oxygen compounds. The behavior of the paraffin and unsaturated hydrocarbons will be considered first.

Dr. David T. Day early observed that the unsaturated hydrocarbons are less diffusible than the paraffin hydrocarbons. Later, Gilpin and Cram clearly demonstrated that when petroleum is allowed to diffuse through tubes packed with fuller's earth, the unsaturated hydrocarbons collect in the earth of lower sections of the tubes, while the paraffins tend to accumulate in the lightest fraction at the top of the tube. In the present investigation, these results have been fully confirmed. On pages 296 to 299 are given the bromine absorption values, and the percentages by volume absorbed by concentrated sulphuric acid of the various oils obtained from definite sections of a tube. These figures indicate conclusively that the amount of unsaturated hydrocarbons in the oils from the lower sections of the tube is much greater than the amount of these hydrocarbons in the lightest fractions at the top of the tube. Furthermore, the bromine absorption values for the oils of similar fractions of the first, second, and third frac-

tionation, given on page 298, show that in the progress of the fractionation more and more of the unsaturated hydrocarbons are removed. Herr,¹ in Russia, has likewise observed that these hydrocarbons are less diffusible than the paraffins.

An interesting confirmation in Nature of these experiments has been recently presented by Clifford Richardson and K. G. MacKenzie.² They found that a colorless natural naphtha from the Province of Santa Clara, Cuba, contained practically no unsaturated hydrocarbons, but was almost entirely a mixture of naphthenes and paraffins. Concentrated sulphuric acid absorbed but 0.76 per cent. by volume, while fuming sulphuric acid absorbed only 1.8 per cent. With the naphtha were obtained water and an emulsion of water, oil and clay. These investigators are of the opinion that the naphtha was "undoubtedly formed by the upward filtration of heavy petroleum through the clay stratum, similar to the fuller's earth filtrations of Gilpin and Cram, and the light naphtha in the upper part of the stratum was afterwards partly liberated by saline waters, the oil remaining in the clay forming with water the emulsion."²

A comparison of the proportions of unsaturated hydrocarbons in Ohio and Pennsylvania oils shows that the latter contains a much smaller percentage of these hydrocarbons. By assuming that the Pennsylvania oil diffused upward through such porous media as shales and limestones to its present location in the sandstones, it is possible to account for the smaller amounts of the olefins in it on the basis of the experimental work described above. In its passage through the capillary interstices of the clays, limestone and sandstones, a fractionation, resulting in the removal of the unsaturated hydrocarbons, probably occurred. It is reasonable to conclude, therefore, that the variation in the content of unsaturated hydrocarbons between the Ohio, Texas, and California oils, on the one hand, and the Pennsylvania oil on the other, can be probably accounted for by assuming that the latter was subjected to capillary diffusion at some time in its career.

¹ Petroleum, August, 1909.

² Am. J. Sci., May, 1910.

That the light-colored naphthas occurring in various parts of the world were originally darker and heavier oils, and that their primitive character was changed by diffusion through media possessing the power of fractionation, seems very probable.

The behavior of the aromatic hydrocarbons, in particular benzene, in passing through fuller's earth, constitutes one of the subjects of this investigation. The results of this study, given in detail on pages 269 to 276, indicate clearly that benzene, like the olefins, tends to collect in the lower sections of a tube of fuller's earth through which the benzene, in solution, is allowed to diffuse. That the aromatic hydrocarbons in the natural oil behave in a similar manner has not yet been decided. The proportion of these hydrocarbons in the Illinois oil investigated was too small to enable us to determine accurately their amounts in the various fractions obtained by the capillary diffusion of the crude oil. The ordinary methods, such as nitration with a mixture of nitric and sulphuric acids, and sulphonation, employed for the quantitative determination of the aromatic hydrocarbons, could not be used in this work, owing to the fact that these reagents readily affect the unsaturated hydrocarbons as well. A study of the conduct of the aromatic hydrocarbons in the natural oil containing large amounts of them will be undertaken in the near future. It is probable, however, that the benzene and homologous compounds in crude petroleum behave like the unsaturated hydrocarbons.

The presence of larger amounts of aromatic hydrocarbons in the Ohio than in the Pennsylvania petroleum, and still larger amounts in the California and Texas oils, seems to afford further evidence in favor of the view that the Pennsylvania oil has undergone much greater diffusion, and consequently greater fractionation, than any of the other oils.

The conduct of the sulphur compounds in petroleum in the process of diffusion is similar to that of the unsaturated hydrocarbons. On pages 298 to 299, the percentages of sulphur present in the oils from different parts of the tube and different

stages of fractionation are tabulated. One series of figures will be given to show the behavior of the sulphur compounds:

Lot 6. Fraction A	Per cent. of sulphur.	
	First fractionation.	Third fractionation.
" B	0.04	0.003
" D	0.05	...
" E	0.09	...
	0.16	...

It is clear from these figures that the sulphur compounds, like the unsaturated hydrocarbons, tend to collect in the lower sections of a layer of fuller's earth through which petroleum is allowed to diffuse.

In 1902, Clifford Richardson and E. C. Wallace,¹ in an investigation on the occurrence of free sulphur in Beaumont petroleum, passed this oil upward through the kaolin filter described by Dr. D. T. Day at the Petroleum Congress in Paris, in 1900, and obtained a distinct fractionation. The percentages of sulphur in the crude oil, and the oils obtained by this fractionation were determined. The results are given in the following table:

	Sp. gr. 25°/25°.	Per cent. sulphur.
Crude oil	0.9140	1.75
1st fraction	0.8775	0.70
2nd fraction	0.8986	0.91
3rd fraction	0.9038	1.04

It seems reasonable to assume from these results that the variations in the sulphur content between the Pennsylvania and Ohio oils may be satisfactorily explained by the view that the former oil, as previously stated, diffused from other regions to its present location, and in its migration a large part of its original content of sulphur was removed. Further work upon this point will be undertaken in this laboratory.

No careful study of the behavior of the nitrogen and oxygen compounds in petroleum diffusing through a porous medium has as yet been undertaken. A careful investigation of this matter will be pursued in this laboratory later on.

¹ J. Soc. Chem. Ind., March, 1902.

It is probable that such an investigation will show that the nitrogen compounds conduct themselves like the sulphur and unsaturated compounds.

The Object of this Investigation.

The present investigation was undertaken for the immediate purpose of studying the changes occurring in the crude Illinois oil when allowed to diffuse through fuller's earth. The more distant, but more fundamental, object was to gain further insight into the causes of the variations between the various oils of this country.

EXPERIMENTAL.

Preliminary Experiments.

The Relative Amounts of Oil Lost in Heated and Unheated Fuller's Earth.—Before the actual investigation of the Illinois oil was undertaken, experiments were made to determine the relative amounts of oil lost in heated and unheated fuller's earth.¹ In the work of Gilpin and Cram, the earth was always heated until geysers ceased to form, and then allowed to cool for several hours. The purpose of heating the earth was to obtain larger yields of oil, but towards the close of their investigation it became apparent that the amount of oil lost in unheated fuller's earth was not as large as they had supposed it to be. Since much time and labor is consumed in the process of heating and then cooling the earth, it seemed advisable to settle this point at the outset.

Apparatus.—The apparatus employed for this investigation was essentially the same as that used by Gilpin and Cram. *A, A, A, A* (Fig. 1) are tin reservoirs made to hold somewhat more than a liter. The tin tubes *B, B, B, B*, 5.5 feet in length, and 1.25 inches in diameter, rest upon narrow tin supports placed upon the bottom of the reservoirs, and are connected with the branched glass tube *F* by suction tubing fitted with pinchcocks at *E, E, E, E*. The tube *F* is connected with the large tank *C*, which serves to maintain fairly constant pressures; *C* is in turn joined by the glass tube *D*

¹ The fuller's earth employed in these investigations was generously supplied by the Atlantic Refining Company of Philadelphia.

to a manometer, and the latter connected with the Chapman pump. Any number of these tubes may be set up in series under the same diminished pressure.

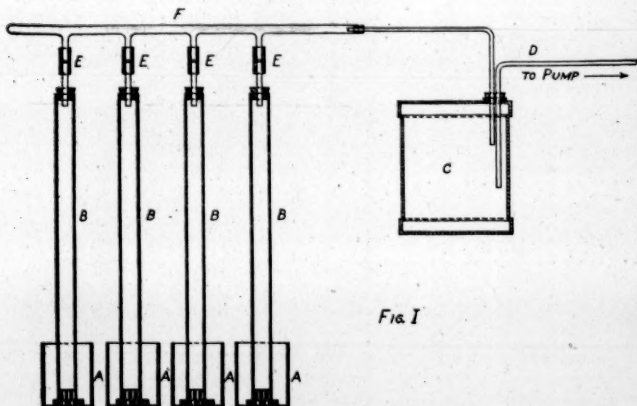


Fig. I

After the tubes are closed at their lower ends with grooved corks covered with muslin to prevent the earth from sifting out, they are packed to the desired firmness with the fuller's earth. Each tube is then placed in its own reservoir, containing the oil to be fractionated. When they are connected to the branched tube *F*, the pressure in the system of tubes is reduced by the suction pump. The oil rises at first rapidly, then its diffusion gradually diminishes in power. When the reservoirs are almost exhausted, the tubes are disconnected and clamped, with the bottom ends up, above shorter tubes of the same diameter, into which the oil-laden earth is allowed to slide. These shorter tubes are made of two curved pieces, joined at the bottom by a cap, and held together at the top by a ring. The cylinders are opened by slipping off the ring and cap and removing one of the curved pieces, and the earth divided into the desired sections. When water is added in

portions to the earth and the two mixed thoroughly, the oil is displaced and is drawn off in separate portions.

Six tubes packed with heated fuller's earth were set up alternately with six tubes filled with the unheated earth. Each tube was placed in its own reservoir containing 950 cc. of crude oil. The oil was allowed to diffuse upward through the tubes under diminished pressure. Sixteen hours elapsed before the oil in the reservoirs was exhausted. Since the tubes did not rest directly upon the bottom of the reservoirs, a small amount of oil remained, the volume of which was subtracted from the volume originally supplied. The earth from each tube was shaken into a bucket, and the oil recovered by displacement with water, as described above. The results of these experiments are given in the following table:

Table I.—Heated Fuller's Earth.

Tubes.	Weight of fuller's earth. Grams.	Oil absorbed by earth. cc.	Oil recovered. cc.	Oil lost. cc.	Per cent. oil lost. cc.
1	1005	850	450	390	46
3	1000	792	460	332	41
5	1035	850	500	350	41
7	1070	865	450	415	48
9	1035	813	430	383	47
11	1045	885	530	355	41
Total, ...		5055	2830	2225	44

Unheated Fuller's Earth.

2	1075	917	585	332	36
4	1095	853	562	291	34
6	1065	840	500	340	42
8	1045	814	435	379	46
10	1035	873	510	363	41
12	1055	850	485	365	41
Total, ...		5147	3077	2070	40

The petroleum employed in the above experiments was a dark, green oil from Venango County, Pennsylvania, possessing a specific gravity of 0.810.

Since the Illinois oil, which was used in the fractionation proper, described later, differs materially from the Pennsyl-

vania petroleum, further experiments were undertaken to determine the relative amounts of this oil retained by heated and unheated earth.

Ten tubes, five of which were packed as uniformly as possible with fuller's earth that had been heated until geysers ceased to form, and the other five with unheated earth, were placed in reservoirs, each containing 950 cc. of Illinois oil, specific gravity 0.8375. When the oil was entirely absorbed, the tubes were taken down and the oil-laden earth shaken into two breakable cylinders and divided into the following sections: *A* constitutes the section, 10 cm. in length, measured downward from the level to which the oil had ascended; *B*, the next 15 cm.; *C*, 20 cm.; *D*, 30 cm.; *E*, 35 cm.; the remainder of the earth to the bottom of the tube, designated as *F*, was entirely discarded.

The earth was then treated with separate portions of water. The oils displaced by the successive additions of water were collected separately and are designated in the table below as *A*₁, *A*₂, *B*₁, *B*₂, and so on; *A*₁ is the oil first displaced, *A*₂ the oil next expelled by further additions of water. The volumes and specific gravities of the recovered oils were determined. The results are given in the following table:

Table II.

Heated fuller's earth.			Unheated fuller's earth.	
Frac.	Spec. grav.	Vol. cc.	Spec. grav.	Vol. cc.
<i>A</i> ₁	0.8287	100	0.8320	72
<i>A</i> ₂			0.8352	22
<i>B</i> ₁	0.8390	157	0.8405	184
<i>B</i> ₂	0.8485	35	0.8451	124
<i>C</i> ₁	0.8441	280	0.8443	270
<i>C</i> ₂	0.8507	67	0.8495	147
<i>D</i> ₁	0.8450	393	0.8483	368
<i>D</i> ₂	0.8490	132	0.8517	210
<i>E</i> ₁	0.8537	339	0.8500	360
<i>E</i> ₂	0.8564	174	0.8569	185
		1701	1942	

These results indicate that unheated fuller's earth retains no more oil than the heated earth. Although, in these ex-

periments, the percentage of oil lost in the unheated is smaller than that lost in the heated earth, Gilpin and Cram, employing heated earth, recovered, in one test, 5,951 cc. from 9,070 cc., and, in another, 5,415 cc. from 8,915 cc., the amount of oil lost in the earth in the first test corresponding to 34 per cent., in the second to 39 per cent. It is clear, therefore, that there is no sufficient, if any, compensation for the time and labor spent in heating the earth. In the investigations that followed, herefore, the unheated fuller's earth was always used.

The Diffusion of Benzene in Solution through Fuller's Earth.—In order to deal more intelligently with the fractionation of the crude Illinois petroleum, it seemed advisable to study the behavior of the individual aromatic hydrocarbons, especially benzene, both alone and mixed with paraffin hydrocarbons, when allowed to diffuse upward through fuller's earth. Gilpin and Cram established the fact that the paraffin hydrocarbons tend to collect in the lightest fractions at the top of the tube. Their method consisted in distilling by heat six samples of oils of different specific gravities, each 300 cc. in volume, and collecting ten fractions between definite intervals. Five of these samples consisted of oil partly fractionated by fuller's earth, and the other of the crude oil. The specific gravity and viscosity of each fraction were determined; then to 30 cc., or to all there was where the amount was less than 30 cc., an equal volume of concentrated sulphuric acid (specific gravity 1.84) was added, and the two shaken in a machine for half an hour or longer. The volume of the oil unaffected by the acid was measured, and, by subtraction, the volume of oil absorbed was calculated. This latter volume represents only approximately the percentage of unsaturated hydrocarbons present in the oil, because sulphuric acid of this strength readily dissolves benzene when the two are thoroughly shaken.

In this investigation various solutions of benzene and a refined paraffin oil, boiling between 160° and 240°, and only slightly attacked by sulphuric acid, were made up and allowed to rise in tubes packed with unheated fuller's earth. The

pressure in the system was reduced very little, because the liquid, under a greatly diminished pressure, rose too rapidly. About 24 hours elapsed before the oil in the reservoirs was exhausted.

The earth in each tube was shaken out and divided into six sections. Beginning at the uppermost point to which the oil had ascended, grade *A* consisted of the first 8 cm.; grade *B* of the next 8 cm., grade *C* of 18 cm.; grade *D* of 30 cm.; grade *E* of 35 cm.; and, finally, grade *F* of the remainder of the earth, depending on the height to which the oil had ascended. This division is the same as that used by Gilpin and Cram. The oil in the earth was displaced by water and drawn off.

The specific gravity of each fraction was determined by means of the Mohr-Westphal balance at exactly 20°. The fourth decimal is not to be considered as strictly accurate, but gives a closer approximation to the truth than if it were entirely discarded.

The viscosity was determined by means of the viscosometer described by Ostwald and Luther and modified by Jones and Veazey.¹ The time taken for measured volumes of the oils to drain from the small bulb, whose capacity was 4.5 cc., was compared with the time required for a similar amount of water to run through. These values were substituted in the equation

$$\gamma = \gamma_0 \frac{TS}{T_0 S_0},$$

where γ_0 = coefficient of viscosity of water. For this, 0.01002, the value obtained by Thorpe and Rodger,² was used.

t = time of flow of liquid under examination.

S = specific gravity, measured at 20°, of liquid under examination.

T_0 = time of flow of water.

S_0 = specific gravity of water. Since the balance was calibrated for water, at 20°, the value for S is unity.

γ = coefficient of viscosity of oil under examination.

¹ Z. physik. Chem., **61**, 351.

² Phil. Trans., A, **185**, 397 (1894).

The amount of benzene present in each fraction was determined by shaking the oil with an excess of ordinary concentrated sulphuric acid (specific gravity 1.84) for periods of time varying from 30 to 60 minutes, until there was no further diminution in the volume of the oil.

The following experiments demonstrate the power of this acid to dissolve benzene, forming benzenesulphonic acid:

(1) Twenty-five cc. of benzene were shaken vigorously in a machine with 25 cc. of concentrated sulphuric acid (specific gravity 1.84) for 30 minutes. Amount of benzene dissolved, 7 cc., or 28 per cent.

(2) Twenty-five cc. were shaken for 30 minutes with 50 cc. of acid. Amount of benzene dissolved, 18 cc., or 72 per cent.

(3) Twenty-five cc. were shaken for 30 minutes with 75 cc. of acid. Amount of benzene dissolved, 25 cc., or 100 per cent.

The reagents usually employed for removing benzene are a mixture of fuming nitric and concentrated sulphuric acids. The work of Worstall,¹ Francis and Young,² and others, shows that such a mixture readily attacks the paraffin hydrocarbons, especially at higher temperatures, forming nitro derivatives, and also oxidizing them to a considerable extent. Furthermore, in working with this mixture the oil must be kept at a low temperature to prevent a violent reaction which results usually in the decomposition of the oil. In this work, therefore, in order to avoid the danger of attacking the paraffin hydrocarbons, and for the sake of convenience, concentrated sulphuric acid was used.

It seems advisable, at this point, to call attention to the fact that the power of ordinary concentrated sulphuric acid to remove benzene and homologous hydrocarbons has been generally overlooked. In order to determine the percentages of these hydrocarbons, it is customary to shake the oils to be analyzed with concentrated sulphuric acid, and then to nitrate the unaffected oil. It is assumed that the acid removes such substances as the unsaturated hydrocarbons, and does not attack the aromatic hydrocarbons. Thus, P.

¹ THIS JOURNAL. 20, 202; 21, 210.

² J. Chem. Soc., 1898, 928.

Poni,¹ in determining the presence and percentage of aromatic hydrocarbons in Roumanian petroleum, collected fractions between 35° and 70°, distilled under diminished pressure. These were purified by shaking with sulphuric acid, and each nitrated with a mixture of 1 part of nitric acid (specific gravity 1.52) and 2 parts sulphuric acid (specific gravity 1.8). The recovered oils were assumed to be paraffins and naphthenes, while the proportion of benzene and unsaturated hydrocarbons was calculated from the nitro products obtained. It is obvious from the results obtained in the present work that some of the benzene was removed in the process of purifying the fractions. The amount dissolved would depend upon the vigor of the shaking and its duration, as well as on the strength of the sulphuric acid. It is highly probable, therefore, that his percentage of benzene is too low.

In the study of the mixture of benzene and paraffin hydrocarbons, twenty-five cc. of each fraction, or the whole fraction when it was less than 25 cc., were shaken vigorously with three times their volume of concentrated sulphuric acid for 30 minutes. The amount unabsorbed was measured over the acid in a burette, after sufficient time was allowed for most of the oil that was mechanically held in suspension to rise. The oil was then reshaken with a little more acid 15 minutes longer, and the volume again read. In cases where the benzene was present only in small quantities one shaking was sufficient, in other cases it was repeated a second time.

The paraffin oil employed, specific gravity 0.797, was shaken several times with fresh portions of concentrated sulphuric acid until the acid was no longer colored, and only a slight diminution in volume occurred when a small sample of the oil was thoroughly shaken in a machine for some time with the acid. The oil was then washed with water and sodium hydroxide and dried over calcium chloride. The specific gravity decreased to 0.792.

When this oil was mixed with benzene in various propor-

¹ Ann. Sci. Univ. Jassy. 1907, 192-202 (abstracted in J. Chem. Soc., 92, II. 883 (1907)).

tions, and allowed to diffuse upward through fuller's earth, the following results, arranged in series, were obtained:

Table III.

Series 1.—Oil alone. Specific gravity 0.792 Level of oil, 28 cm.

Grade.	Volume of oil, cc.	Specific gravity.	Viscosity.	Per cent. benzene. ²
A	11	0.789		
B	17	0.792		
C	60	0.7912	0.0154	
D	100	0.7915	0.0140	
E	150	0.7913	0.0134	
F	139	0.7915	0.0134	

Orig. vol., $\frac{477^1}{778}$

Series 2.—90 per cent. oil (0.792)—10 per cent. benzene (0.8775).
Specific gravity, 0.7983. Level of oil, 22 cm.

Grade.	Volume of oil, cc.	Specific gravity.	Viscosity.	Per cent. benzene.
A	11	0.787		10.0
B	16	0.7923		13.3
C	56	0.7935	0.0131	11.6
D	109	0.7943	0.0123	14.8
E	145	0.7957	0.0120	14.4
F	245	0.7955	0.0116	14.8

Orig. vol., $\frac{582}{872}$

The results that are tabulated in the various series are expressed diagrammatically in the following curves. The ordinates represent the different grades of oil, and the abscissas, the percentages of benzene and the specific gravities.

¹ The original volumes of solution vary with each series, owing to the fact that more or less always remained behind in the reservoir below the level of the tin support. In Series 1, 2, 3, and 4, 950 cc. were supplied to each reservoir; in the rest of the series, each reservoir contained originally 1,000 cc.

² In this series the percentages of benzene are not given, because the paraffin oil alone was used.

The final curve represents *in toto* the results of the experimental work upon the diffusion of benzene in solution through fuller's earth. The ordinates of this curve represent the percentages of benzene, and the abscissas, the various mixtures of benzene and oil that were allowed to diffuse through the earth.

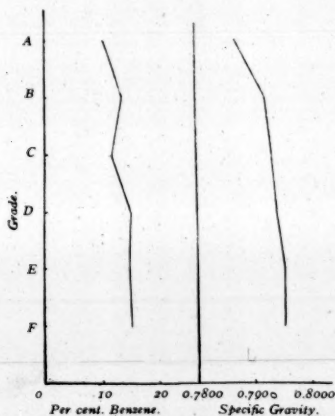


Fig II. Series 2.

Series 3.—80 per cent. oil (0.792)—20 per cent. benzene (0.8775).
Specific gravity, 0.806. Level of oil, 25 cm.

Grade.	Volume of oil, cc.	Specific gravity.	Viscosity.	Per cent. benzene.
A	25	0.7948	0.0147	15.3
B	35	0.7981	0.0130	16.0
C	78	0.8017	0.0117	22.4
D	126	0.8005	0.0105	21.6
E	166	0.801	0.0107	22.4
F	146	0.798	0.0110	20.8

Orig. vol., 576
892

Series 4.—75 per cent. oil (0.792)—25 per cent. benzene (0.8775).

Specific gravity, 0.810. Level of oil, 33 cm.

Grade.	Volume of oil, cc.	Specific gravity.	Viscosity. ¹	Per cent. benzene.
A	16	0.800		22.0
B	35	0.803	0.0129	23.3
C	74	0.8077	0.0126	24.0
D	128	0.805	0.0114	24.0
E	152	0.8068	0.0102	26.0
F	120	0.8065	0.0105	28.0

Orig.-vol., 525
655

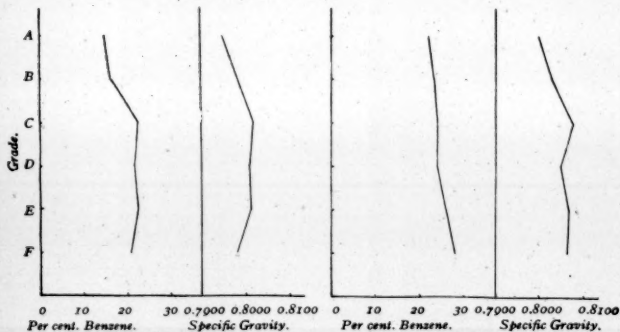


Fig. III. Series 3.

Fig. IV. Series 4.

Series 5.—75 per cent. oil (0.794)²—25 per cent. benzene (0.8775). Specific gravity, 0.8115. Level of oil, 24 cm.

Grade.	Volume of oil, cc.	Specific gravity.	Viscosity.	Per cent. benzene.
A	25	0.7942	0.0123	14.0
B	28	0.8048	0.0104	21.2
C	70	0.8105	0.0094	31.2
D	140	0.8100	0.0094	27.6
E	172	0.8100	0.0094	32.0
F	144	0.8093	0.0095	27.6

Orig. vol., 579
875

¹ The viscosities of Grades A and B in a few of the tables are not given, because, in these series, which were the first to be made, the decision to determine the viscosities was reached only after the fractions had been treated with acid. Since A and B were small, all the oil was used up in this treatment.

² In Series 5, 8, 9 and 10 the specific gravity of the refined oil is 0.794. Since the quantity of oil of specific gravity 0.792 was not sufficient for all the series, a second quantity was prepared which had the specific gravity 0.794. This oil was used in the above-mentioned series.

Series 6.—75 per cent. oil (o. 792)—25 per cent. benzene (o. 8775).

Specific gravity, 0.8083. Level of oil, 27 cm.

Grade.	Volume of oil, cc.	Specific gravity.	Viscosity.	Per cent. benzene.
A	22	0.7995	0.0106	17.5
B	32	0.8055	0.0099	24.4
C	82	0.8052	0.0100	24.0
D	155	0.8085	0.0093	28.8
E	190	0.8085	0.0093	31.2
F	93	0.8063	0.0096	28.8

Orig. vol., 574
923

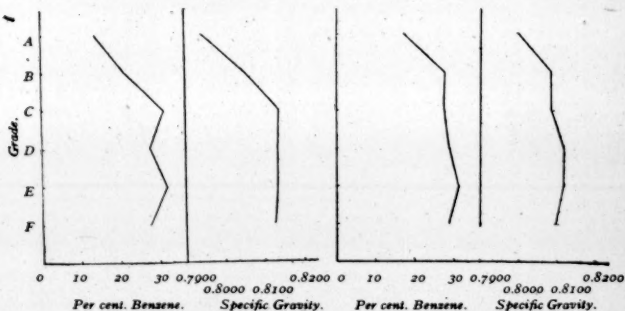


Fig. V. Series 5.

Fig. VI. Series 6.

Series 7.—59.5 per cent. oil (o. 792)—40.5 per cent. benzene (o. 8775). Specific gravity, 0.8223. Level of oil, 9 cm.

Grade.	Volume of oil, cc.	Specific gravity.	Viscosity.	Per cent. benzene.
A	9 ¹			
B	15	0.8069		14.0
C	48	0.816	0.0103	22.4
D	96	0.8182	0.0086	31.2
E	160	0.820	0.0082	31.6
F	255	0.8185	0.0083	29.6

Orig. vol., 583
922

¹ In Series 7 the volume of Grade A recovered was so small that no measurements could be made.

Series 8.—50 per cent. oil (0.794)—50 per cent. benzene (0.8775).

Specific gravity, 0.8295. Level of oil, 17 cm.

Grade.	Volume of oil, cc.	Specific gravity.	Viscosity.	Per cent. benzene.
A	22	0.8122		24.5
B	32	0.819		28.4
C	78	0.8287	0.0077	44.8
D	111	0.8275	0.0077	47.6
E	155	0.827	0.0077	39.2
F	192	0.8256	0.0079	36.4

Orig. vol., 590
960

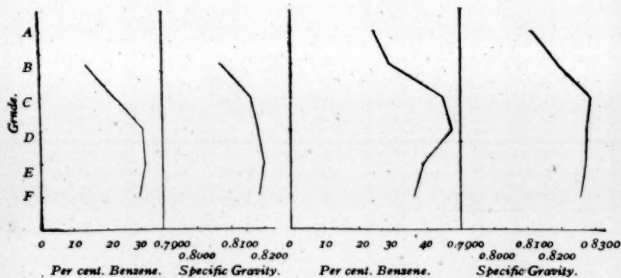


Fig. VII. Series 7.

Fig. VIII. Series 8.

Series 9.—50 per cent. oil (0.794)—50 per cent. benzene (0.8775).

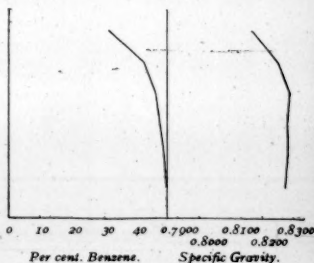
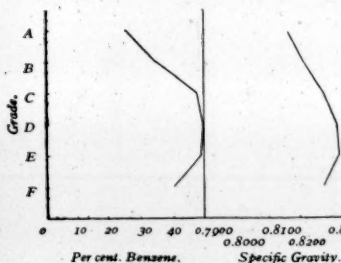
Specific gravity, 0.8315. Level of oil, 18 cm.

Grade.	Volume of oil, cc.	Specific gravity.	Viscosity.	Per cent. benzene.
A	18	0.816	0.0091	26.0
B	24	0.8210	0.0085	34.5
C	76	0.8275	0.0078	47.6
D	136	0.8283	0.0077	50.0
E	174	0.8293	0.0076	49.2
F	144	0.8277	0.0078	40.0

Orig. vol., 572
923

Series 10.—50 per cent. oil (0.794)—50 per cent. benzene (0.8775). Specific gravity, 0.8295. Level of oil, 16 cm.

Grade.	Volume of oil, cc.	Specific gravity.	Viscosity.	Per cent. benzene.
A	31	0.8135	0.0097	31.6
B	45	0.8251	0.0081	43.6
C	85	0.8290	0.0076	46.4
D	140	0.8280	0.0077	47.6
E	175	0.8285	0.0076	49.6
F	137	0.8272	0.0076	50.0
		613		
Orig. vol.,		972		



Series 11.—75 per cent. crude oil (0.810)—25 per cent. benzene (0.8775). Specific gravity, 0.8312. Level of oil, 18 cm.

Grade.	Volume of oil, cc.	Specific gravity.	Viscosity.	Per cent. benzene. ¹
A	12	0.8255	0.0445	
B	22	0.8268	0.0423	
C	52	0.8280	0.0300	
D	76	0.8290	0.0298	
E	140	0.8300	0.0263	
F	186	0.8320	0.0276	
		488		
Orig. vol.,		890		

¹ The percentages of benzene in Series 11, in which crude oil was employed, are not recorded, because, owing to the formation of heavy black emulsions, the loss in volume could not be determined with any degree of accuracy.

Series 12.—Benzene alone (0.8775). Level of oil, 33 cm.

Grade.	Volume of oil, cc.	Specific gravity.	Viscosity.	Per cent. benzene.
A	16	0.8765		
B	15	0.877		
C	68	0.878	0.0066	
D	128	0.8778	0.0066	
E	157	0.8775	0.0066	
F	89	0.8771	0.0066	

Orig. vol., $\frac{473}{888}$

An examination of these figures shows conclusively that benzene tends to collect in the lower portions of the tube. The specific gravities and viscosities confirm the results obtained by determining the percentages of benzene present by removing the benzene with concentrated sulphuric acid. The specific gravities of Grades *F* to *C* run very close together, and are all much greater than those of Grades *A* and *B*. Since benzene possesses a high specific gravity (in this work the specimen had a specific gravity of 0.8775), the larger value for the lower grades indicates the presence of larger amounts of benzene. The specific gravity of the paraffin oil was only 0.792, showing that the higher specific gravities were due to larger percentages of benzene. Further, since the viscosity of the benzene used was 0.0066, and that of the paraffin oil about 0.0150, the viscosities of those fractions containing higher percentages of benzene, we should expect, ought to be much smaller than those containing less benzene. The results show that the viscosities of the grades *F* to *C* are much smaller than those of *A* and *B*.

It will be observed that the maximum in specific gravity is reached, not at *F*, as might be expected in the fractionation of the crude oil, but between *C* and *D*. Between *B* and *C* there is a marked decrease. This sudden break is found also in the viscosities, and in the percentages of benzene. While the sharp breaks in the curves represent the marked change in the proportion of benzene and the height to which it rises in the tube, no satisfactory explanation has yet been ob-

tained as to why it should occur at these points. This action will be studied more carefully later.

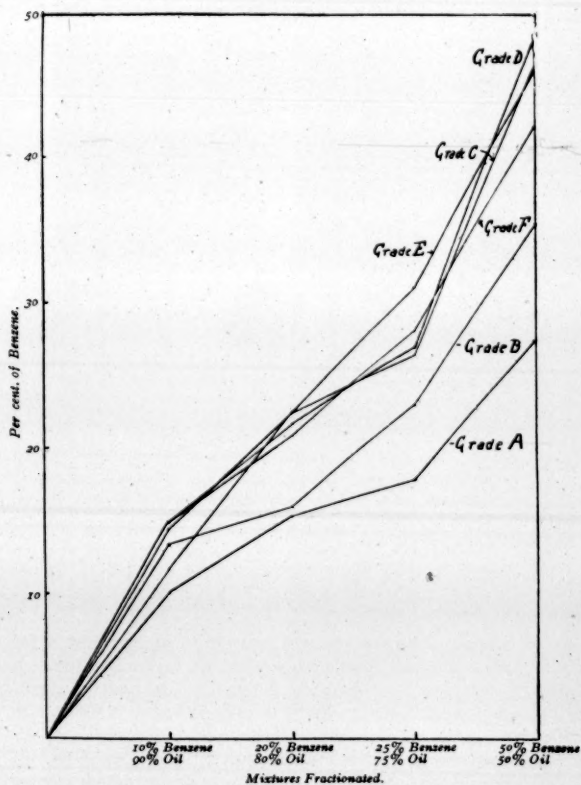


Fig. XI.

In order to determine the degree of exactness of the percentages of benzene obtained, known amounts of benzene were added to the oil until the specific gravity corresponded closely to that obtained by fractionation. The amount of benzene thus added and the amount actually removed by the acid agree very closely, as the following results show:

Benzene in 25 cc. of mixture.		Benzene found in the grades of Series 8. cc.	
	Specific gravity.		Specific gravity.
7.3	0.8143	Grade A 7.9	0.8135
9.4	0.8213	" B 10.9	0.8251
11.1	0.8274	" F 12.5	0.8272
11.3	0.8287	" E 12.4	0.8287
11.9	0.8293	" C 11.6	0.8290

The variations in the specific gravities of the mixtures and those of the grade A-F are due to the fact that in the latter series some fractionation had taken place, and therefore the paraffin oils mixed with the benzene were not identical with those mixed with the benzene in the series of prepared mixtures, as the paraffin oil used was not an individual substance but a mixture.

The Fractionation of Crude Petroleum.

The petroleum employed for the fractionation was an oil obtained from the E. E. Newlin farm, 2.5 miles west of Robinson, Crawford County, Illinois. The specific gravity of the oil was 0.8375 at 20°; its color was dark brown.

The fractionation of the oil was effected by upward diffusion through tubes packed with fuller's earth. In order to shorten the time required for the oil to diffuse by capillarity to the upper parts of the tube, the fine interstices and pores of the earth were evacuated by applying diminished pressure at the top of the tube. By this aid, the time required for the oil to reach the top of a tube was reduced from several weeks to one or two days.

The apparatus employed is the same as that described on page 261.

The tin tubes were packed as uniformly as possible by introducing definite amounts of earth, and ramming solidly

with rods tipped with rubber stoppers. The degree of compactness depended upon the kind of oil to be used. For the crude oil, about one and one-half feet of the tube was filled at a time, and the earth packed as firmly as possible; for the lighter oils, one foot of the tube was filled at a time; for the oils heavier than the crude, between two and three feet of the tube were filled at one time.

The tubes were then placed individually in reservoirs containing 950 cc. of the crude oil, after which diminished pressure was applied at the top of the tubes. The oil rose rapidly at first, then diffused more and more slowly as the tops of the tubes were approached. When the oil in the reservoirs was completely exhausted, the tubes were disconnected from the branched glass tube *F* (see Fig. 1) and the oil-laden earth shaken into two breakable cylinders. For the various fractions, the following divisions of the earth were made: Fraction *A* constituted the first 10 cm., measured downward from the level to which the oil had ascended; fraction *B*, the next 15 cm.; *C*, 20 cm.; *D*, 30 cm.; *E*, 35 cm., and *F*, the remainder to the bottom of the tube. In the first fractionation up to Lot 28, fraction *F* was discarded; from Lot 28 to the end of the first fractionation, *E* and *F* were collected together.

After thus dividing the earth, the various portions were placed in separate receptacles and treated with water. After each addition of water the two were thoroughly mixed. The earth, when the oil first appears, is granular; as more water is added, liberating more oil, the earth becomes muddy, and when as much oil as possible has been expelled by the water, the earth has the consistency of glue.

The portions of oil liberated by successive additions of water were collected separately. As Gilpin and Cram¹ pointed out, the oil that is first expelled, if not very small in volume as compared with the oils succeeding, possesses a lower specific gravity than the oil liberated by further additions of water; the latter, in turn, is lighter than the next succeeding oil. The oil that is liberated last, therefore, possesses a higher specific

¹ THIS JOURNAL, 40, 495 (1908).

gravity than any of the oils preceding it. Sometimes, however, the specific gravity remains constant after the second or third extraction. This fractionation, by means of water, was combined with the fractionation effected by the fuller's earth. In the tables that follow, A_1 is the oil first liberated, A_2 the oil next liberated; in the lower fractions, *i. e.*, C , D , E , three and sometimes four extractions were made before all the oil that could possibly be liberated by water was recovered.

The specific gravity of the oils was determined by means of the Mohr-Westphal balance. As mentioned before, the fourth decimal is not to be considered as rigidly accurate, but it gives a closer approximation to the truth than if it were entirely discarded. The temperature at which the specific gravity was measured was exactly 20° .

Table IV.—The First Fractionation.

Lot. No. of tubes.	1		2		3			
	15		5		10			
Hours ¹ req.	12—14 tubes 23—1 tube		16		17—8 tubes		45—2 tubes	
Frac.	Spec. grav.	Vol., ² cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.
A_1	0.8250	312	0.8285	73	0.8223	138	0.8233	50
A_2	0.8287	90	0.8310	59	0.8270	54		
B_1	0.8367	485	0.8370	218	0.8372	258	0.8405	130
B_2	0.8392	250	0.8408	78	0.8400	200		
C_1	0.8413	828	0.8440	272	0.8442	290	0.8505	120
C_2	0.8460	228	0.8442	136	0.8455	235	0.8535	65
C_3	0.8488	126			0.8480	148		
D_1	0.8470	1014	0.8430	313	0.8488	538	0.8546	235
D_2	0.8495	375	0.8464	150	0.8500	295	0.8619	30
D_3	0.8514	200	0.8500	112	0.8540	115		
D_4	0.8555	172						
E_1	0.8527	720	0.8475	285	0.8537	380	0.8615	172
E_2	0.8540	430	0.8509	135	0.8550	245		
E_3	0.8570	400	0.8540	118	0.8580	170		

¹ Chapman pump was run day and night. Manometer indicated pressures ranging from 30 to 80 mm.

² In lots 1 to 5, 1000 cc. of crude oil were supplied to each tube.

Lot. No. of tubes.	4		5		6	
	10		8		10 ¹	
Hours req.	16		17— 7 tubes 24— 1 tube		17— 1 tube ² 40— 3 tubes 96— 1 tube	
					17— 3 tubes 40— 1 tube 150— 1 tube	
Frac.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.
A ₁	0.8295	170	0.8313	130	0.8320	72 ³
A ₂	0.8315	100	0.8357	56	0.8352	22
B ₁	0.8375	327	0.8392	358	0.8405	184
B ₂	0.8413	250	0.8453	92	0.8451	124
C ₁	0.8418	505	0.8419	425	0.8443	270
C ₂	0.8442	223	0.8439	138	0.8495	147
C ₃	0.8495	74	0.8465	130	...	...
D ₁	0.8449	495	0.8454	640	0.8483	368
D ₂	0.8455	328	0.8500	167	0.8517	210
D ₃	0.8490	260	0.8509	195	...	...
E ₁	0.8500	545	0.8495	575	0.8500	360
E ₂	0.8510	295	0.8513	185	0.8569	185
E ₃	0.8567	170	0.8555	130	...	...

Lot. No. of tubes.	7		8		9	
	9		10		10	
Hours req.	20— 7 tubes		20— 1 tube 24— 1 tube		19— 8 tubes 22— 2 tubes	
					24— 2 tubes 40— 8 tubes	
Frac.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.
A ₁	0.8325	66	0.8175	45	0.8364	88
A ₂	0.8356	30	...	...	0.8365	64
B ₁	0.8395	164	0.8333	110	0.8400	215
B ₂	0.8418	140	...	...	0.8420	240
B ₃	...	...	...	...	...	...
C ₁	0.8408	475	0.8417	132	0.8445	368
C ₂	0.8468	123	0.8500	22	0.8467	225
C ₃	...	...	...	...	0.8495	82
D ₁	0.8449	500	0.8468	110	0.8465	460
D ₂	0.8487	270	0.8498	106	0.8478	260
D ₃	...	...	...	...	0.8500	260
E ₁	0.8500	483	0.8533	228	0.8490	450
E ₂	0.8524	318	...	...	0.8495	354
E ₃	...	...	...	...	0.8521	233

¹ Beginning with lot 6, 950 cc. of crude oil were supplied to each tube.

² The pressure in the tubes was diminished intermittently.

³ See page 263.

⁴ See page 263.

⁵ Several cubic centimeters of this fraction were mixed, accidentally, with fraction E₃.

Lot.	10		11		12		13	
No. of tubes	8		10		9		10	
Hours req.	17		17		42		24-8 tubes 40-2 tubes	
Frac.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.
A ₁	0.8273	130	0.8258	215	0.8325	125	0.8323	122
A ₂	0.8288	75	0.8318	70	0.8345	87	0.8352	96
B ₁	0.8395	220	0.8370	340	0.8430	235	0.8438	245
B ₂	0.8418	160	0.8480	180	0.8467	120	0.8470	180
C ₁	0.8423	240	0.8422	488	0.8470	278	0.8464	317
C ₂	0.8440	195	0.8450	205	0.8487	288	0.8505	235
C ₃	0.8500	150	...	...	...	...	...	...
D ₁	0.8460	410	0.8465	565	0.8495	452	0.8500	312
D ₂	0.8475	210	0.8490	310	0.8522	305	0.8492	375
D ₃	0.8500	348	0.8530	187	...	...	0.8518	150
E ₁	0.8532	320	0.8510	297	0.8505	475	0.8505	450
E ₂	0.8535	282	0.8520	405	0.8533	490	0.8489	395
E ₃	0.8550	215	0.8533	155	...	...	0.8518	180

Lot.	14		15		16	
No. of tubes.	5		6		15	
Hours req.	24 ¹		26-3 tubes		40-11 tubes 64-4 tubes	
Frac.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.
A ₁	0.8355	132	0.8381	60	0.8305	73
A ₂	...	...	...	...	...	0.8370
B ₁	0.8470	236	0.8487	94	0.8452	143
B ₂	...	...	...	...	...	0.8357
C ₁	0.8565	98	0.8430	110	0.8465	138
C ₂	0.8560	150	0.8480	57	0.8509	88
C ₃	...	...	...	...	...	0.8449
D ₁	0.8523	170	0.8475	212	0.8505	158
D ₂	0.8550	205	0.8517	104	0.8522	178
D ₃	...	...	...	...	...	0.8445
E ₁	0.8540	150	0.8467	184	0.8561	192
E ₂	0.8532	325	0.8502	152	0.8585	140
E ₃	...	...	...	...	...	0.8475
						0.8509
						0.8562
						0.8575
						0.8540
						0.8530
						0.8575
						0.8538
						0.8562
						0.8595

¹ When the pressure in the tubes was diminished, the oil rose rapidly, and in a short time, the reservoirs were nearly two-thirds exhausted. The pump was stopped, and the remainder of the oil allowed to diffuse during the night under normal pressure.

Lot.	17		18		19		20	
No. of tubes.	9		8		10		10	
Hours req.	40		24—5 tubes 48—2 tubes 64—1 tube		40—8 tubes 64—2 tubes		20—6 tubes 30—4 tubes	
Frac.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.
A	0.8258	225	0.8322	112	0.8320	146	0.8281	236
B	0.8432	452	0.8435	335	0.8438	385	0.8413	518
C ₁	0.8480	450	0.8495	250	0.8480	300	0.8450	350
C ₂	0.8488	168	0.8500	250	0.8472	315	0.8495	300
D ₁	0.8530	520	0.8530	320	0.8509	422	0.8508	325
D ₂	0.8550	350	0.8540	350	0.8535	355	0.8538	460
E ₁	0.8585	385	0.8547	90 ¹	0.8492	580	0.8513	445
E ₂	0.8598	460	0.8526	640	0.8560	415	0.8540	550
Lot.	21		22		23		24	
No. of tubes.	10		10		10		10	
Hours ² req.	24—6 tubes 40—2 tubes 64—2 tubes		40—6 tubes 64—4 tubes		48—5 tubes 72—5 tubes		40—4 tubes 64—6 tubes	
Frac.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.
A	0.8275	245	0.8281	210	0.8241	330	0.8250	287
B	0.8410	615	0.8405	508	0.8395	615	0.8408	535
C ₁	0.8452	520	0.8459	265	0.8448	420	0.8463	475
C ₂	0.8488	226	0.8472	410	0.8470	305	0.8505	186
D ₁	0.8512	533	0.8505	435	0.8533	400	0.8540	525
D ₂	0.8535	415	0.8523	450	0.8541	465	0.8540	360
E ₁	0.8557	375	0.8615	385	0.8650	305	0.8623	393
E ₂	0.8625	282	0.8585	365	0.8624	350	0.8645	335
Lot.	25		26		27		28	
No. of tubes.	9		10		10		10	
Hours ² req.	48—8 tubes 72—1 tube		17—2 tubes 24—4 tubes 41—4 tubes		17—4 tubes 29—6 tubes		24—7 tubes 28—3 tubes	
Frac.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.
A	0.8270	225	0.8284	315	0.8312	230	0.8333	240
B	0.8425	410	0.8422	550	0.8440	470	0.8440	410
C ₁	0.8495	75 ³	0.8473	520	0.8460	400	0.8458	415
C ₂	0.8492	250	0.8508	178	0.8478	232	0.8500	177
D ₁	0.8509	320	0.8515	600	0.8482	435	0.8470	387
D ₂	0.8510	480	0.8540	230	0.8500	420	0.8498	400
E ₁	0.8556	335	0.8559	490	0.8520	465	0.8492	690 ⁴
E ₂	0.8570	395	0.8586	135	0.8565	335	0.8505	600

¹ This irregularity, i. e., the liberation of oil with a specific gravity higher than those of the oils immediately following, is observed when an amount of water is added sufficient to replace a very small amount of oil for the first fraction.

² Pressure in the tubes was diminished intermittently.

³ Some oil of this fraction was lost.

⁴ Beginning with lot 28, fractions E and F were collected together.

Lot. No. of tubes.	29		30		31		32	
	10		15		10		15	
	Hours ¹ req.	18— 5 tubes 40— 5 tubes	20— 7 tubes 41— 6 tubes 63— 2 tubes		44— 4 tubes 89— 6 tubes		40— 7 tubes 89— 4 tubes 103— 4 tubes	
Frac.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.
A	0.8262	300	0.8348	335	0.8292	245	0.8270	445
B	0.8395	505	0.8468	630	0.8439	576	0.8423	726
C ₁	0.8463	390	0.8490	560	0.8495	465	0.8500	730
C ₂	0.8488	270	0.8505	277	0.8523	205	0.8500	220
D ₁	0.8520	510	0.8485	750	0.8517	670	0.8545	750
D ₂	0.8543	290	0.8502	540	0.8552	210	0.8543	540
EF ₁	0.8550	417	0.8520	1125	0.8555	805	0.8580	870
EF ₂	0.8559	645	0.8528	880	0.8610	360	0.8598	910
		3327		5097		3536		5191

Lot. No. of tubes.	33		34		35	
	10		10		9	
	Hours ¹ req.	41— 4 tubes 65— 4 tubes 89— 2 tubes	44— 6 tubes 68— 4 tubes		48— 6 tubes 73— 3 tubes	
Frac.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.
A	0.8330	290	0.8355	320	0.8380	235
B ₁	0.8440	365	0.8475	525	0.8460	452
B ₂	0.8462	165	...	...	...	...
C ₁	0.8502	500	0.8508	470	0.8508	345
C ₂	0.8540	160	0.8543	190	0.8525	245
D ₁	0.8555	655	0.8575	530	0.8549	580
D ₂	0.8562	250	0.8585	325	0.8573	335
EF ₁	0.8575	735	0.8535	895	0.8557	645
EF ₂	0.8585	480	0.8555	405	0.8570	492
		3600		3660		3329

Observations on the First Fractionation.

Specific Gravity.—The range of the specific gravity extended from 0.8175, the value for Fraction A₁ of Lot 7, to 0.8650, the value for Fraction E₁ of Lot 13. The value for the crude oil itself was 0.8375. The limits of the specific gravities of the individual lots averaged from 0.820 to 0.860. The specific gravity decreases gradually from E to B, but between B and A, the decrease, in most of the lots, is much greater

¹ Pressure in tubes was diminished intermittently.

than between any two consecutive lower fractions. This marked change was also observed in the study of the diffusion of benzene in solution. A detailed investigation into the cause of this sudden divergence will be undertaken in the near future.

Color.—The colors of the fractions obtained extended from green to black. The lighter oils possessed a beautiful green fluorescent color, which shaded gradually to brown, and then to the deep black of the heavier oils.

Odor.—The unpleasant odor of the crude petroleum disappeared almost entirely in the oils of Fraction A and B; but the other fractions still possessed to a greater or less extent the odor of the natural oil.

The Volume of Oil Retained by the Fuller's Earth.—The amount of oil retained by the earth averaged about 55 per cent. of the amount supplied. In the first fractionation of the crude Pennsylvania oil, specific gravity 0.810, Gilpin and Cram found that approximately 40 per cent. of the oil was retained by the earth. It is evident, therefore, that the amount of oil remaining in the earth depends chiefly upon the character of the oil. The Pennsylvania petroleum contains a much smaller percentage of unsaturated hydrocarbons, sulphur, and asphaltic substances than the Illinois oil employed in this investigation. Since the fuller's earth, as will be shown later, readily removes these substances in the process of fractionation, the large percentage of Illinois oil retained by the earth is thus clearly explained. It is safe to conclude that if the heavy Texas or California oil were allowed to diffuse through fuller's earth, the amount of oil retained would exceed the amounts of either of the above-mentioned oils lost in the earth.

The Second Fractionation.

The products obtained from the first fractionation were united according to the following arrangement:

Lot.	Specific gravity of the oils united.	Specific gravity of mixture.
36	0.8250-0.8350	0.8293
37	0.8350-0.8400	0.8390
38	0.8400-0.8450	0.8433
39	0.8400-0.8450	0.8433
40	0.8450-0.8500	0.8490
41	" "	"
42	" "	"
43	" "	"
44	0.8500-0.8600	0.8543
45	" "	"
46	" "	"
47	" "	"
48	" "	"
49	" "	"
50	" "	"

The oils thus combined were subjected to chilling and filtration for the purpose of removing as much dissolved paraffin as possible. The procedure was as follows: The oils were first chilled at temperatures ranging from 0° to 10° and then filtered through plaited filter papers. When the oil ceased to drip from the funnel, the residue upon the filter paper was placed in a larger filter press, and the remaining oil separated by pressure from the paraffin. The filter press was simple in construction. A piston, fitted closely in an iron cylinder, was gradually forced down upon the oil-laden paraffin, which rested upon a membrane of cotton duck fastened between perforated tin supports. The retained oil was forced through the membrane and was collected from the outlet below. The lighter oils deposited very little paraffin; from the heavier ones somewhat more paraffin was separated. Owing to the high viscosity of the heavier oils, the filtration proceeded very slowly. Since too much time was consumed in this process, the paraffin of some of the oils of Fraction *E* was not removed. A slight change in specific gravity occurred in the oils from which the paraffin was removed.

The final specific gravities of the united oils were as follows:

Lot.	Specific gravity.	
36	0.8305	Paraffin removed.
37	0.8415	" "
38	0.8433	Paraffin not removed.
39	0.8455	Paraffin removed.
40	0.8515	" "
41	0.8515	" "
42	0.8515	" "
43	0.8540	" "
44	0.8543	Paraffin not removed.
45	0.8543	" " "
46	0.8543	" " "
47	0.8543	" " "
48	0.8543	" " "
49	0.8557	Paraffin removed.
50	0.8557	" "

When these oils were again allowed to diffuse upward through fuller's earth, the following fractionation was obtained:

Table V.—The Second Fractionation.

Lot.	36		37		38		39	
No. of tubes.	5		4		8		8	
Hours ¹ req.	44—3 tubes 48—2 tubes		51		48—7 tubes 64—1 tube		29—4 tubes, 45—3 tubes, 64—1 tube.	
Frac.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.
A	0.8272	160	0.8292	135	0.8331	180	0.8290	255
B ₁	0.8315	216	0.8421	215	0.8447	175	0.8432	355
B ₂	0.8331	58			0.8455	210	0.8458	110
C ₁	0.8334	350	0.8467	295	0.8490	305	0.8492	455
C ₂	0.8355	85			0.8505	175	0.8513	180
D ₁	0.8330	360	0.8468	340	0.8492	400	0.8505	740
D ₂	0.8339	320	0.8485	152	0.8509	295	0.8527	275
EF ₁	0.8347	720	0.8480	535	0.8508	710	0.8546	1166
EF ₂	0.8356	320	0.8489	215	0.8518	355	0.8560	350
	2589		1887		3886		2805	

¹ In this series, as well as those following, the pressure in the tubes was diminished intermittently.

Lot.	40		41		42		43	
No. of tubes.	9		5		5		4	
Hours req.	48—5 tubes 72—4 tubes		40		69		10 days—2 tubes. 17 days—2 tubes.	
Frac.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.
A	0.8305	380	0.8316	235	0.8325	210	0.8435	65
B ₁	0.8438	515	0.8460	290	0.8487	265	0.8546	115
B ₂	0.8453	155	0.8480	65	0.8515	54	...	...
C ₁	0.8518	600	0.8523	375	0.8540	335	0.8575	200
C ₂	0.8539	170	0.8540	100	0.8567	56	...	...
D ₁	0.8550	685	0.8558	470	0.8572	420	0.8605	220
D ₂	0.8560	330	0.8571	110	0.8582	175	0.8640	50
EF ₁	0.8605	780	0.8620	580	0.8640	675	0.8650	225
EF ₂	0.8620	600	0.8622	320	0.8650	200	0.8615	78
	4215		2545		2420		953	

Lot.	44		45		46		47	
No. of tubes.	3		5		5		5	
Hours req.	48—2 tubes 96—1 tube		66		93		13 days ¹	
Frac.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.
A	0.8330	85	0.8362	170	0.8332	210	0.8340	145
B ₁	0.8505	175	0.8510	210	0.8480	260	0.8500	275
B ₂	...	...	0.8522	80	0.8505	50	...	...
C ₁	0.8582	155	0.8562	265	0.8554	300	0.8553	320
C ₂	0.8605	65	0.8585	50	0.8567	95	0.8576	50
D ₁	0.8605	195	0.8567	425	0.8600	370	0.8595	430
D ₂	0.8620	120	0.8580	100	0.8613	120	0.8618	70
EF ₁	0.8672	240	0.8659	615	0.8666	610	0.8665	330
EF ₂	0.8680	175	0.8670	150	0.8680	130	0.8670	215
	1210		2065		2145		1835	

¹ Owing to the weakness of the water pressure, the pressure in the tubes was only slightly diminished. The tubes were taken down before the reservoirs were completely exhausted. The distances to which the oil had risen were 35, 25, 30, 20, 10 cm. from the tops of the tubes.

Lot.	48		49		50	
No. of tubes.	5		7		5	
Hours req.	14 days ¹		48		72—4 tubes. 80—1 tube.	
Frac.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.
A	0.8385	125	0.8341	255	0.8320	170
B ₁	0.8530	275	0.8505	395	0.8485	230
B ₂			0.8520	95	0.8500	70
C ₁	0.8568	320	0.8560	380	0.8565	300
C ₂	0.8586	90	0.8572	230	0.8577	100
D ₁	0.8610	325	0.8620	500	0.8609	480
D ₂	0.8623	115	0.8625	290	0.8626	125
EF ₁	0.8695	330	0.8705	500	0.8685	640
EF ₂	0.8700	80	0.8705	580	0.8700	235
		1660		3225		2350

Observations on the Second Fractionation.

Specific Gravity.—The range of the specific gravities grows smaller as the oils to be fractionated become lighter, and less complex. Thus, in Lot 36, the range of specific gravity extends from 0.8272, the value for Fraction A, to 0.8356, the value for EF₂, the difference between them being 0.0084. In Lot 38, the mother oil, of specific gravity 0.8433, yielded fractions whose specific gravities ranged from 0.8331 to 0.8518, amounting to a difference of 0.0187. This fact appears to be general throughout the various lots, and points to the gradual formations of mixtures which will pass through the earth unaltered, just as the fractionation by distillation tends to yield substances with definite boiling points.

Color.—The color of the oils in this fractionation shaded from a very light yellow to greenish black.

Odor.—The odor of the crude petroleum vanished completely from the oils of this fractionation.

Volume of Oil Retained by the Earth.—The oil retained by the earth in this fractionation amounted to approximately

¹ Owing to the weakness of the water pressure, the pressure in the tubes was diminished but slightly during this time. The tubes were taken down before the reservoirs were completely exhausted. The distances to which the oil had risen were 30, 35, 30, 60, 55 cm. from the tops of the tubes.

50 per cent., a smaller percentage, as is naturally to be expected, than in the fractionation of the crude petroleum.

The Third Fractionation.

The following oils obtained from the second fractionation were united for the third fractionation:

Lot 51.—Specific Gravity 0.8316.

Lot.	Fraction.	Specific gravity.	Volume, cc.	Lot.	Fraction.	Specific gravity.	Volume, cc.
36	A	0.8272	160	42	A	0.8325	210
39	A	0.8290	255	44	A	0.8330	85
37	A	0.8292	135	36	B ₂	0.8331	58
40	A	0.8305	380	38	A	0.8331	180
36	B ₁	0.8315	216	46	A	0.8332	210
41	A	0.8316	235	36	C ₁	0.8334	350
50	A	0.8320	170	49	A	0.8341	255

2899

Lot 52.—Specific Gravity 0.8343.

Lot.	Fraction.	Specific gravity.	Volume, cc.	Lot.	Fraction.	Specific gravity.	Volume, cc.
36	D ₁	0.8330	360	36	EF ₁	0.8347	720
36	D ₂	0.8339	320	36	EF ₂	0.8356	320
47	A	0.8340	145	36	C ₂	0.8355	85

1950

Lot 53.—Specific Gravity 0.8433.

Lot.	Fraction.	Specific gravity.	Volume, cc.	Lot.	Fraction.	Specific gravity.	Volume, cc.
45	A	0.8362	170	38	B ₁	0.8447	175
48	A	0.8385	125	40	B ₂	0.8453	155
37	B ₁	0.8421	215	38	B ₂	0.8455	210
39	B ₁	0.8432	355	39	B ₂	0.8458	50
40	B ₁	0.8438	515				

1970

Lot 54.—Specific Gravity 0.8473.

Lot.	Fraction.	Specific gravity.	Volume, cc.	Lot.	Fraction.	Specific gravity.	Volume, cc.
39	B ₂	0.8458	60	50	B ₁	0.8485	230
41	B ₁	0.8460	290	42	B ₁	0.8487	265
37	C ₁	0.8467	295	39	C ₁	0.8492	455
41	B ₂	0.8480	65	38	C ₁	0.8490	305

1965

Lot 55.—Specific Gravity 0.8485.

Lot.	Fraction.	Specific gravity.	Volume, cc.	Lot.	Fraction.	Specific gravity.	Volume, cc.
37	D_1	0.8468	340	37	EF_2	0.8489	215
37	D_2	0.8485	152	38	D_1	0.8492	400
37	EF_1	0.8480	535	47	B_1	0.8500	275

1917

Lot 56.—Specific Gravity 0.8508.

Lot.	Fraction.	Specific gravity.	Volume, cc.	Lot.	Fraction.	Specific gravity.	Volume, cc.
50	B_2	0.8500	70	45	B_1	0.8510	210
49	B_1	0.8505	395	39	C_2	0.8513	180
44	B_1	0.8505	175	42	B_2	0.8515	54
46	B_2	0.8505	50	40	C_1	0.8518	600
38	C_2	0.8505	175				

1909

Lot 57.—Specific Gravity 0.8509.

Lot.	Fraction.	Specific gravity.	Volume, cc.	Lot.	Fraction.	Specific gravity.	Volume, cc.
39	D_1	0.8505	740	38	D_2	0.8509	295
38	EF_1	0.8508	710	38	EF_2	0.8518	355

2100

Lot 58.—Specific Gravity 0.8558.

Lot.	Fraction.	Specific gravity.	Volume, cc.	Lot.	Fraction.	Specific gravity.	Volume, cc.
49	B_2	0.8520	95	49	C_1	0.8560	380
45	B_2	0.8522	80	45	C_1	0.8562	265
41	C_1	0.8523	375	50	C_1	0.8565	300
48	B_1	0.8530	275	42	C_2	0.8567	56
40	C_2	0.8539	170	46	C_2	0.8567	95
42	C_1	0.8540	335	48	C_1	0.8568	320
41	C_2	0.8540	100	49	C_2	0.8572	230
47	C_1	0.8553	320	43	C_1	0.8575	200
46	C_1	0.8554	300				

3896

Lot 59.—Specific Gravity 0.8563.

Lot.	Fraction.	Specific gravity.	Volume, cc.	Lot.	Fraction.	Specific gravity.	Volume, cc.
39	EF_1	0.8546	1166	41	D_2	0.8571	110
40	D_1	0.8550	685	42	D_1	0.8572	420
41	D_1	0.8558	470	45	D_2	0.8580	100
39	EF_2	0.8560	350	42	D_2	0.8582	175
40	D_2	0.8560	330	48	C_2	0.8586	90
45	D_1	0.8567	425	47	D_1	0.8595	430

4750

Lot 60.—Specific Gravity 0.8615.

Lot.	Fraction.	Specific gravity.	Volume, cc.	Lot.	Fraction.	Specific gravity.	Volume, cc.
46	D_1	0.8600	370	41	EF_1	0.8620	580
49	EF_1	0.8605	780	44	D_2	0.8620	120
43	D_1	0.8605	220	49	D_1	0.8620	500
44	D_1	0.8605	195	41	EF_2	0.8622	320
50	D_1	0.8609	480	48	D_2	0.8623	115
48	D_1	0.8610	325	49	D_2	0.8625	290
46	D_2	0.8613	120	50	D_2	0.8626	125
47	D_2	0.8618	70	42	E_1	0.8640	675
40	EF_2	0.8620	600				
							5880

Lot 61.—Specific Gravity 0.8680.

Lot.	Fraction.	Specific gravity.	Volume, cc.	Lot.	Fraction.	Specific gravity.	Volume, cc.
42	EF_2	0.8650	200	46	EF_2	0.8680	130
43	EF_1	0.8650	225	44	EF_2	0.8680	175
45	EF_1	0.8659	615	50	EF_1	0.8685	640
47	EF_1	0.8665	330	48	EF_1	0.8695	330
46	EF_1	0.8666	610	50	EF_2	0.8700	235
47	EF_2	0.8670	215	49	EF_1	0.8705	500
45	EF_2	0.8670	150	49	EF_2	0.8705	580
44	EF_1	0.8672	240				
							4975

The oils thus united were fractionated by fuller's earth again, with the results given in Table VI.

Table VI.—The Third Fractionation.

Lot. No. of tubes. Hours req.	51		52		53		54	
	3 ¹		2		2		2	
	60		60		48		48	
Frac.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.
A	0.8213	92	0.8219	65	0.8266	73	0.8303	66
B	0.8303	185	0.8333	143	0.8431	115	0.8488	115
C_1	0.8337	165	0.8375	190	0.8464	175	0.8518	175
C_2	0.8345	90	...	...	...	...	...	...
D_1	0.8353	210	0.8388	188	0.8468	145	0.8523	160
D_2	0.8356	170	0.8393	90	0.8474	115	0.8528	105
E_1	0.8366	385	0.8403	175	0.8473	202	0.8530	245
E_2	...	...	0.8411	92	0.8488	73	0.8548	60
F_1	0.8373	190	0.8431	88	0.8496	170	0.8548	145
		1487			1031			1068
								1091

The tin tubes used in these lots were 1.5 inches in diameter.

Lot.	55		56		57		58	
No. of tubes.	2		2		2		4	
Hours req.	48—1 tube 72—1 tube		96		96		72—3 tubes 90—1 tube	
Frac.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.
A	0.8283	58	0.8313	75	0.8336	55	0.8318	170
B	0.8457	100	0.8488	135	0.8491	130	0.8531	260
C ₁	0.8515	155	0.8546	170	0.8528	180	0.8578	205
C ₂	...	...	...	...	...	...	0.8592	105
D ₁	0.8521	220	0.8553	150	0.8551	185	0.8588	205
D ₂	0.8543	50	0.8560	92	0.8573	45	0.8593	340
E ₁	0.8540	270	0.8553	145	0.8568	170	0.8603	325
E ₂	...	...	0.8563	90	0.8588	70	0.8613	170
F	0.8566	180	0.8575	130	0.8611	170	0.8628	275
	1033		987		1005		2055	

Lot.	59		60		61	
No. of tubes.	5		6		5	
Hours req.	72		72		5 days. ¹	
Frac.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.
A	0.8328	195	0.8343	195	0.8413	...
B	0.8508	340	0.8540	330	0.8601	...
C ₁	0.8578	325	0.8601	290	0.8683	...
C ₂	0.8588	112	0.8618	130	...	...
D ₁	0.8608	490	0.8628	440	0.8709	...
D ₂	0.8623	135	0.8638	85	...	...
E ₁	0.8628	475	0.8664	425	0.8688	...
E ₂	0.8633	155	0.8683	140	...	...
F	0.8673	330	0.8703	310	0.8691	...

Observations on the Third Fractionation.

Specific Gravity.—The decrease in the range of specific gravity as the oils supplied become lighter is observed in this fractionation as in the preceding ones.

Color.—The lightest oils were almost colorless; the heavier oils were dark brown to green.

Odor.—Most of the oils possessed an agreeable odor.

Prolonged Diffusion.—In Lot 61, the time required for the oils to reach the tops of the tubes was five days. No fractionation, as is evident from an examination of the specific

¹ The pressure in the tubes was diminished intermittently.

² See below, this page.

gravities, occurred in the lower parts of the tubes. The heavier oils of fractions *D*, *E*, and *F* were exceedingly viscous.

Volume of Oil Retained by the Earth.—The volume of oil retained by the earth in this fractionation amounted to approximately 45 per cent. The increase in the yield of oil indicates, therefore, a process of purification, in which, as will be shown later, such compounds as the unsaturated hydrocarbons are removed.

The Fourth Fractionation.

The following fractions obtained from the third fractionation were united for the fourth fractionation:

Lot 62.—Specific Gravity 0.8298.

Lot.	Fraction.	Specific gravity.	Volume, cc.	Lot.	Fraction.	Specific gravity.	Volume, cc.
51	A	0.8213	92	51	B	0.8303	185
52	A	0.8219	65	56	A	0.8313	75
53	A	0.8266	73	58	A	0.8318	170
55	A	0.8283	66	59	A	0.8328	195
54	A	0.8303	58				
							979

Lot 63.—Specific Gravity 0.8343.

Lot.	Fraction.	Specific gravity.	Volume, cc.	Lot.	Fraction.	Specific gravity.	Volume, cc.
52	B	0.8333	143	51	C ₂	0.8345	90
57	A	0.8336	55	51	D ₁	0.8353	210
51	C ₁	0.8337	185	51	D ₂	0.8356	170
60	A	0.8343	195				
							1048

Lot 64.—Specific Gravity 0.8368.

Lot.	Fraction.	Specific gravity.	Volume, cc.	Lot.	Fraction.	Specific gravity.	Volume, cc.
51	E ₁	0.8366	388	52	C ₁	0.8375	190
51	F	0.8372	190	52	D ₁	0.8388	188
							956

Lot 65.—Specific Gravity 0.8430.

Lot.	Fraction.	Specific gravity.	Volume, cc.	Lot.	Fraction.	Specific gravity.	Volume, cc.
52	D ₂	0.8393	90	52	F	0.8431	88
52	E ₁	0.8403	175	55	B ₁	0.8457	100
52	E ₂	0.8411	92	53	C ₁	0.8464	175
53	B ₁	0.8431	115	53	D ₁	0.8468	145
							980

Lot 71.—Specific Gravity 0.8638.

Lot.	Fraction.	Specific gravity.	Volume, cc.	Lot.	Fraction.	Specific gravity.	Volume, cc.
59	D_2	0.8623	135	60	D_2	0.8638	85
60	D_1	0.8628	440	59	E_2	0.8633	155
59	E_1	0.8628	475	60	E_1	0.8664	425
58	F	0.8628	375				
							1990

Table VII.—The Fourth Fractionation.

Lot.	62		63		64		65	
No. of tubes.	1		1		1		1	
Hours req.	72		72		90		48	
Frac.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.
A	0.8243	32	0.8273	45	0.8297	41	0.8308	42
B	0.8298	71	0.8357	75	0.8378	57	0.8428	70
C	0.8323	90	0.8378	95	0.8401	81	0.8463	92
D	0.8330	115	0.8383	130	0.8408	115	0.8473	130
E	0.8333	130	0.8388	98	0.8413	135	0.8471	130
F	0.8341	75	0.8393	95	0.8418	70	0.8483	80
		513		538		499		544

Observations on the Fourth Fractionation.

Specific Gravity.—As in the preceding fractionations, the decrease in the range of specific gravity as the mother oils become lighter is again observed in this fractionation. It is evident, moreover, that there is a constant forward accumulation towards definite and constant mixtures. The lighter oils of one lot are found to possess specific gravities closely approaching those of the heavier oils of the preceding lot.

Color.—The oils of Fraction A were almost colorless; the color of the heavier oils ranges from green to light brown.

Odor.—All the oils of this fractionation possessed agreeable odors.

Volume of Oil Retained.—The volume of oil retained by the earth amounted to approximately 40 per cent.

Deposition of Paraffin.—In Fractions A and B of several of the lots, a fine, crystalline deposit separated out, and collected upon the bottom of the bottles containing the oils.

When the oils were warmed, this deposit dissolved completely, showing it to be paraffin.

Chemical Examination of the Fractionated Oils. Unsaturated Hydrocarbons.

Action of Concentrated Sulphuric Acid.—The percentage of volume of oil absorbed by concentrated sulphuric acid (specific gravity 1.84) was determined according to the following procedure: Ten cc. of the oil to be examined were measured into a glass-stoppered bottle, and thirty cc. of concentrated sulphuric acid were added. The mixture was thoroughly shaken in a machine for thirty minutes and then poured into a burette. After allowing sufficient time for any oil that might be mechanically absorbed in the acid to rise to the top, the volume of unabsorbed oil was read directly over the acid. Owing to the formation of heavy emulsions, no attempt was made to neutralize and wash the oil.

The results of the analyses are given in the table below:

Lot.	Fraction.	Per cent. by volume absorbed.	Lot.	Fraction.	Per cent. by volume absorbed.
51	A	2.3	51	D ₁	11.5
51	B	6.1	51	D ₂	12.0
51	C ₁	9.1	51	E	12.5
51	C ₂	10.2	51	F	14.5

Action of Bromine.—The method employed for determining the amount of bromine absorbed by the oils was as follows: Between 0.5 and 0.9 of a gram of the oil to be examined was dissolved in 10 to 15 cc. of carbon tetrachloride. Five cc. of a standard solution of bromine in carbon tetrachloride were then introduced, and the solution allowed to remain, with occasional shaking, in a dark place for 30 minutes. Ten cc. of a 10 per cent. solution of potassium iodide were then added, and the amount of iodine liberated determined immediately by titrating with a standard solution of sodium thiosulphate. A few drops of a starch solution were introduced to mark accurately the end of the titration. The amounts of bromine absorbed by addition and substitution were not estimated separately.

The amounts of bromine absorbed, calculated upon the basis of 100 grams of oil, are given in the following table:

Table VIII.—First Fractionation.

Lot.	Fraction.	Per cent. of bromine absorbed.	Lot.	Fraction.	Per cent. of bromine absorbed.
32	A	5.02	32	D	7.87
32	B	6.96	32	E	8.00
32	C	7.40	Crude oil		7.64

Second Fractionation.

Lot.	Fraction.	Per cent. of bromine absorbed.	Lot.	Fraction.	Per cent. of bromine absorbed.
36	A	4.74	36	D ₁	6.81
36	B ₁	5.40	36	D ₂	6.28
36	B ₂	5.66	36	EF ₁	6.49
36	C ₁	5.56	36	EF ₂	7.18
36	C ₂	6.18			

Third Fractionation.

Lot.	Fraction.	Per cent. of bromine absorbed.	Lot.	Fraction.	Per cent. of bromine absorbed.
51	A	3.27	51	D	4.92
51	B	4.36	51	E	4.71
51	C	4.47	51	F	5.36

Fourth Fractionation.

Lot.	Fraction.	Per cent. of bromine absorbed.	Lot.	Fraction.	Per cent. of bromine absorbed.
62	A	2.86	62	E	3.73

These results demonstrate conclusively that the unsaturated hydrocarbons tend to collect in the lower sections of a layer of fuller's earth through which the oil is allowed to diffuse. These figures confirm the results obtained by Gilpin and Cram in their work on the Pennsylvania petroleum. In their investigation, distillation by heat was employed in order to obtain fractions that could be readily studied. In this work the relative amounts of the unsaturated hydrocarbons in the various oils were determined directly as they came from the earth.

The percentages by volume of oil absorbed by concentrated sulphuric acid represent only approximately the per-

centages of unsaturated hydrocarbons, since, as was shown previously, any benzene which may have been present in the oils was also removed by the concentrated acid. This fact rendered impossible a quantitative separation of the aromatic from the unsaturated hydrocarbons. Since no other methods, besides nitration and sulphonation, neither of which could be here employed, were available, no results as to the relative amounts of the aromatic hydrocarbons in the various fractions could be obtained.

It is evident from the results of the bromine determinations that, as the fractionation proceeds, the amounts of unsaturated hydrocarbons become smaller and smaller. A comparison of the amounts of bromine absorbed by Fraction A of the first, second, third and fourth fractionations is given below for the purpose of bringing out this point more clearly:

Per cent. of Bromine Absorbed by Fraction A.

First fractionation.	Second fractionation.	Third fractionation.	Fourth fractionation.
5.02	4.74	3.27	2.86

Sulphur Compounds.—The sulphur in the various oils was determined by the usual method of combustion. For these determinations, the oils obtained from one tube of Lot 6 were employed. The results are given in the following table:

Lot 6 Fraction.	Specific gravity.	Per cent. sulphur.	Lot 6 Fraction.	Specific gravity.	Per cent. sulphur.
A	0.8195	0.04	D	0.8510	0.09
B	0.8362	0.05	E	0.8600	0.16
C	0.8440	Lost			

The percentage of sulphur in the Fractions A, C and E of Lot 51 was also determined. The results were as follows:

Table X.—Lot 51.

Fraction.	Per cent. of sulphur.	Fraction.	Per cent. of sulphur.
A	0.003	E	0.006
C	0.040		

These results show that the sulphur tends to collect in the oils in lower sections of the tube. As the fractionation proceeds, the proportion of sulphur becomes smaller. The figures below indicate that as the oil is subjected to repeated fractionations, the sulphur is gradually removed:

Per cent. of Sulphur.

First fractionation.	Second fractionation.	Third fractionation.
Fraction A 0.04		0.003
Fraction E 0.16		0.006
Fraction C	0.08	0.040

Selective Action of Fuller's Earth.

When the earth, from which as much oil as possible has been extracted by prolonged treatment of water, is dried, and then digested with ether, oils of surprisingly high specific gravity and viscosity are obtained.

In the experiments undertaken to study the selective action of fuller's earth, the procedure was as follows: The earth under examination was thoroughly treated with water until no more oil appeared. This muddy earth of the consistency of thin liquid paste was spread upon porous plates and allowed to dry at room temperature. Several weeks usually elapsed before the earth became completely dry. It was then finely pulverized, and after being thoroughly soaked and shaken with ether the mixture was allowed to remain undisturbed for 24 hours or more. The mixture was then filtered and the dissolved oil recovered by distilling off the ether from the filtrate. The residual earth was then digested with ether for some time by means of an electric stove that completely surrounded the flask. The oil thus extracted was added to the oil first obtained. In several cases the residual earth was treated further with ether in the Soxhlet extractor.

The results of these extractions are given in the following table:

Table XI.

Lot.	Fraction.	Specific gravity at 50°.	Lot.	Fraction.	Specific gravity at 50°.
7	A	0.8470	25	A ₃	0.8391
8	A	0.8502	25	B	0.8489
18	A ₁	0.8419		Specific gravity at 20°.	
18	A ₂	0.8400	51	A	0.8368
19	A ₁	0.8495	51	B	0.8473
19	A ₂	0.8495	51	C	0.8491
19	A ₃	0.8600	51	D	0.8568
25	A ₁	0.8363	51	E	0.8518
25	A ₂	0.8381	51	F	0.8553

The specific gravity of none of the oils of the first and second fractionation, extracted with ether, except those of Lot 19, could be determined at 20° C. All were extremely viscous; those of Lot 25 were so viscous at this temperature that they would not flow when the bottles containing them were inclined. The color of the oils ranges from brown to black. The ethereal solutions, however, of many of the oils were very light in color.

It is interesting to compare the specific gravities of the oils extracted with ether with those of the corresponding oils extracted with water. For this purpose, the oils extracted by water and by ether from the earth of Lot 51 are chosen. In the table below, the specific gravities of these oils at the same temperature, *i. e.*, 20°, are given:

Table XII.—Lot 51. Specific Gravity at 20°.

Frac.	Ether.	Water.	Frac.	Ether.	Water.
A	0.8368	0.8213	D	0.8568	0.8353
B	0.8473	0.8303	E	0.8518	0.8366
C	0.8491	0.8337	F	0.8553	0.8373

As the figures above indicate, the specific gravities of oils extracted with ether are much higher than those of the corresponding oils extracted with water. The presence of such heavy and viscous oils in the upper sections of the tube can be explained only by assuming that they were carried to these heights in solution with the lighter oils, and were then removed by the earth. Since such viscous oils are totally unable to diffuse by capillarity to any appreciable extent, it is not probable that their transportation to the upper parts of the tube was effected by capillary diffusion.

Chemical Examination of the Oils Extracted by Ether—Unsaturated Hydrocarbons.

Action of Concentrated Sulphuric Acid.—The percentage by volume of oil absorbed by concentrated sulphuric acid (specific gravity 1.84) was determined according to the following procedure: Ten cc. of the oil to be examined were measured into a glass-stoppered bottle, and thirty cc. of concentrated sulphuric acid were added. The mixture was thoroughly shaken

in a machine for 30 minutes and then poured into a burette. After allowing sufficient time for any oil that might be mechanically absorbed in the acid to rise to the top, the volume of unabsorbable oil was read directly over the acid. Owing to the formation of heavy emulsions, no attempt was made to neutralize and wash the oil.

The oils selected for examination were those extracted by ether from the earth of Lots 36 and 51.

The results of the analyses are given in the following table:

Table XIII.

Lot.	Fraction.	Oils extracted by ether. Per cent. by volume	Oils extracted by water. Per cent. by volume	Lot.	Fraction.	Oils extracted by ether. Per cent. by volume	Oils extracted by water. Per cent. by volume
		absorbed.	absorbed.			absorbed.	absorbed.
36	A	24.0	3.0	51	C	17.0	9.1
36	B	37.0	10.4	51	D	16.4	11.5
51	A	7.0	2.3	51	E	16.5	12.5
51	B	11.5	6.1	51	F	18.0	14.5

Action of Bromine.—The method employed for determining the amount of bromine absorbed by the oils has already been described (p. 296).

The amounts of bromine absorbed, calculated upon the basis of 100 grams of oil, are given in the table below. The values for the corresponding oils extracted with water are also given for comparison.

Table XIV.

Lot.	Fraction.	Oils extracted by ether. Per cent. of bromine	Oils extracted by water. Per cent. of bromine	Lot.	Fraction.	Oils extracted by ether. Per cent. of bromine	Oils ex- tracted by water. Per cent. of bromine
		absorbed.	absorbed.			absorbed.	absorbed.
32	A	5.30	5.02	51	B	4.45	4.36
32	B	7.39	6.96	51	C	6.27	5.03
36	A	5.72	4.74	51	D	6.09	4.92
36	B	6.10	5.40	51	E	5.98	4.71
36	C	6.72	5.56	51	F	5.20	5.36
51	A	3.27	3.27				

As these results clearly demonstrate, fuller's earth retains the unsaturated hydrocarbons, thus exercising a selective action.

Sulphur Compounds.—The sulphur in the oils obtained by extraction with ether was determined by the usual method of combustion. The results are given in the table below:

Table XV.

Lot 51.	Oils extracted by ether. Per cent. of sulphur.	Oils extracted by water. Per cent. of sulphur.	Lot 51.	Oils extracted by ether. Per cent. of sulphur.	Oils extracted by water. Per cent. of sulphur.
A	0.004	0.003	D	0.060	...
B	0.011	...	E	0.080	...
C	0.050	0.040	F	0.080	0.006

The selective action of the earth, in regard to the sulphur compounds, is indicated by these results. This fact was also pointed out by Richardson and Wallace. It is very probable that the earth also retains largely the nitrogen compounds in the oil, and may also remove to a greater or less extent the benzene hydrocarbons.

These results seem to furnish evidence in favor of the view that the Illinois oil diffused, at some time in the history, through porous media, which exercised a selective action upon it, removing a large part of the unsaturated and sulphur compounds, and probably the benzene and nitrogen compounds.

SUMMARY.

1. When a solution of benzene and a paraffin oil is allowed to diffuse upward through a tube packed with fuller's earth, the benzene tends to collect in the lower sections and the paraffin oil in the upper sections of the tube.
2. When crude petroleum diffuses upward through a tube packed with fuller's earth, a fractionation of the oil occurs. The oil that is displaced by water from the earth from the top of the tube possesses a lower specific gravity than the oil obtained from the earth at the bottom of the tube.
3. As the fractionation proceeds, the range of specific gravity covered in succeeding fractionations becomes smaller, indicating a movement towards the production of mixtures which will finally pass through the earth, unaltered.
4. In the fractionation of petroleum by capillary diffusion through fuller's earth, the amounts of unsaturated hydrocar-

bons and sulphur compounds in the resulting fractions increase gradually from the lightest oils at the top to the heavier oils at the bottom of the tube.

5. Fuller's earth tends to retain the unsaturated hydrocarbons and sulphur compounds in petroleum, thus exercising a selective action upon the oil.

REVIEW.

FIRST YEAR CHEMISTRY. A Text in Elementary Chemistry for Secondary Schools. By WILHELM SEGERBLUM, A.B., Instructor in Chemistry at the Phillips Exeter Academy. Exeter, N. H.: Exeter Book Publishing Co. 1909. pp. xxv + 410.

This book includes the entire work of a year. In 390 pages it contains 169 experiments, some chemical history, nearly as much theory as the average first-year college manual, and a small amount of chemical fact. Cut out one-half of the experiments and replace them by descriptive text, and we should get a very good college manual, but then the book would be like many others. The originality of this book lies in leaving out the descriptive text.

The author says in the preface: "My object has been to give the student a conception of chemistry from the point of view of the scholar and the thinker, rather than from the point of view of the crammer, *i. e.*, to teach chemistry rather than to teach a text-book."

Brave words! but surely some others who have written books for this purpose are also scholars and thinkers. Then why did they include descriptive chemistry instead of making their books like this? Simply to give a well-balanced course instead of an ill-balanced course. Every one recognizes the predominant value of laboratory work and gives as much of it as possible.

A few words regarding the relations of school to college may seem a digression but are not. With the present just complaints about the length of the course, school—college—professional work, it is essential to avoid overlapping between school and college, an evil very noticeable in chemistry. Many students entering the average first-year college chemical course have studied little or no chemistry, others more and some nearly enough to pass the course. Those who know nothing of chemistry have to work hard; those who half-know it all waste their time to their detriment.

The secondary school should send the boy to college either

entirely without education in chemistry or with enough to pass off the first-year college chemistry by examination at entrance.

The amount of labor and intelligence demanded for the study of Mr. Segerblom's book is fully equal to that required in the average first-year college chemistry course, but owing to his desire to avoid "teaching a text-book" much that is necessary is omitted. As an example take the author's treatment of nitrogen, ammonia, nitric acid and nitrates. There is no mention of nitrogen in animal or vegetable life, no mention of ammonia being a decomposition product of animal or vegetable substances or of coal, no mention of nitrogen or any compound of nitrogen as plant food, no mention of gunpowder or of the presence of nitrogen in explosives.

In brief, Mr. Segerblom's method is such that the student on entering college would need much of the first-year college chemistry and yet would be over-trained in certain directions for that course, while with suitable guidance and the same amount of labor the student could have done this college work in school and passed it off on entering college.

As a matter of fact, Exeter, the reviewer believes, has a two-years' course in chemistry, so that the author could so arrange the second year's course that the two years would form a harmonious whole. The criticism offered would not apply to such a case, but the author offers the text to the public for use in secondary schools, and says nothing in the preface about further school work. The great majority of secondary schools give only one year to chemistry, and the criticism applies to the use of the book in such schools.

E. R.

ERRATUM.

P. 134, l. 15, 64.60 should be 84.60.